

COUPLING REACTIONS OF CHLOROFLUORO AND PERFLUOROALKYL IODIDES

Ivan WCLASSICS^{1,*} and Vito TORTELLI²

Solvay Solexis, Viale Lombardia, 20; 20021 Bollate (MI), Italy;

e-mail: ¹ ivan.wclassics@solvay.com, ² vito.tortelli@solvay.com

Received April 30, 2008

Accepted August 25, 2008

Published online December 15, 2008

Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.

Coupling reactions of chlorofluoro- and perfluoroalkyl iodides R_f-I with $R_f = ClCF_2CFCl-$, $(CF_2)_3CF_2-$, $ClCF_2CFCIO(CF_2)_3CF_2-$, $ClCF_2CFCl-$, $(CF_3)_2CF-$, $(CF_3)_2CFCF_2CF_2-$ in the presence of a zinc/solvent system give dimers in good yields. Both homodimerizations (one iodide) and heterodimerizations (two different iodides) have been studied. The effect of temperature and solvent is shown. The zinc mediated dechlorination of vicinal chlorine atoms in the dimers afforded terminal alkenes and dienes.

Keywords: Dimerization; Chlorofluoroalkyl iodides; Perfluoroalkyl iodides; Dehalogenation; Perfluorodiene.

Due to the relatively low dissociation energies of alkyl halides and in particular perfluoroalkyl iodides¹ their radical homo- and heterocoupling reactions²⁻⁵ are an attractive and easy synthetic method for obtaining dimers bearing the same or different end groups. These dimers are valuable synthetic intermediates for perfluorinated terminal alkenes and dienes which can be used as modifiers of fluorinated materials⁶.

In this work, the coupling reactions of some chlorofluoro- and perfluoroalkyl iodides in the presence of zinc and a solvent will be presented and discussed. The experimental conditions are critical: the reaction temperature and solvent effects are particularly important and can change significantly the chemoselectivity.

RESULTS AND DISCUSSION

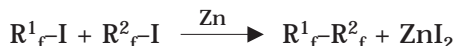
Dimerization Reactions

Both homodimerizations (symmetrical) and heterodimerizations (asymmetrical, cross) of fluorinated alkyl iodides are reactions promoted by a mixture of a metal and acetic anhydride (Ac_2O) under mild conditions^{4,5}. The literature reports several other methods used in coupling iodides: photochemical⁷, electrochemical⁸ and in the presence of copper^{2,3,9}. The photochemical method has the main disadvantage of being very slow, while the Cu-mediated dimerization requires particularly high reaction temperatures (120–200 °C); the electrochemical method requires a sophisticated apparatus and is not particularly suited for laboratory applications. The Zn-mediated dimerization of fluorinated alkyl iodides was therefore the method of choice in this work due to its feasibility on the laboratory scale.

Homodimerizations involve the coupling of two identical fluoroalkyl iodides. They proceed smoothly with high yield and selectivity.



Instead, heterodimerizations involve the dimerization of two different fluorinated alkyl iodides. This will inevitably lead to the formation of a statistical distribution of the dimers, provided that the reactivities of the iodides are the same.



As will be explained in more detail in the Experimental, the strategy adopted in the synthesis of novel fluorinated alkyl dimers is the coupling of chlorofluoroalkyl iodides in the presence of Zn and acetic anhydride at 40 °C. Subsequent dehalogenation of the coupling products in the presence of Zn in an aprotic polar solvent has been performed as well to obtain interesting terminal perfluoro alkenes and dienes¹⁰. In the course of dimerization of $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_3\text{CF}_2\text{I}$, shown in Scheme 1, either the dehalogenation



SCHEME 1

of the ClCF_2CFCl - end groups or the reduction of the terminal fluorinated iodide, $-\text{CF}_2\text{I}$ to $-\text{CF}_2\text{H}$, could compete with the desired dimerization.

The results shown in Table I demonstrate that the solvent system and the temperature are essential for selective dimerization in competition with dechlorination and reduction.

At 40 °C no dehalogenation of the 1,2-dichlorinated ω -iodide is observed while the reduction of the terminal $-\text{CF}_2\text{I}$ to $-\text{CF}_2\text{H}$ occurs with very low conversion (<5 mole %). A possible reason for the low conversion of the reduction is the low acidity of the hydrogens present in the reaction medium: once the intermediate organometal $-\text{CF}_2\text{ZnI}$ has been formed the solvents CH_2Cl_2 or Ac_2O do not transfer hydrogens. The main role of acetic anhydride is both the activation of the zinc surface to allow its reaction with the alkyl iodide and to provide enough solvent polarity for sufficient reactivity. Omitting Ac_2O from the reaction, no conversion of the fluorinated alkyl iodide to the corresponding dimer is observed. If CH_2Cl_2 is replaced by DMF, still in the presence of acetic anhydride, just a 5% yield of the dehalogenated product is obtained, while the main product is the reduced compound, $\text{R}_f-\text{CF}_2\text{H}$. This behavior suggests that DMF stabilizes the organozinc intermediate so well that it can abstract a proton from the solvent; on the other hand, the other competing reaction, dehalogenation, does not occur because the reaction temperature is too low. In fact, in order to achieve dimerization, the temperature is generally kept between 40 and 50 °C⁴ while for 1,2-dechlorinations it lies between 70 and 80 °C¹⁰ when coordinating solvents such as dimethylformamide or isopropyl alcohol are employed.

TABLE I

Yields (in %) of Zn homodimerization of $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_4\text{I}$ as a function of solvent and reaction temperature

| Products | CH_2Cl_2 | $\text{CH}_2\text{Cl}_2 + \text{Ac}_2\text{O}$ | $\text{DMF} + \text{Ac}_2\text{O}$ | $\text{DMF} + \text{Ac}_2\text{O}$ |
|---|--------------------------|--|------------------------------------|------------------------------------|
| | 40 °C | 40 °C | 40 °C | 80 °C |
| $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_8\text{CFClCF}_2\text{Cl}$ | 0 | 95 | 25 | 8 |
| $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_4\text{I}$ | 95 | 0 | 5 | 5 |
| $\text{CF}_2=\text{CF}(\text{CF}_2)_3\text{CF}_2\text{H}$ | 0 | 0 | 5 | 47 |
| $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_4\text{H}$ | 5 | 5 | 65 | 40 |

The theoretical product distribution of the coupling reaction of two fluoroalkyl iodides of a very similar structure, such as $\text{ClCF}_2\text{CFCl}(\text{CF}_2)_3\text{CF}_2\text{I}$ (a) and $\text{ClCF}_2\text{CFClO}(\text{CF}_2)_3\text{CF}_2\text{I}$ (b), in the absence of side reactions and of particular coordinating solvent effects, should give the statistical 1:2:1 ratio of symmetric (aa):asymmetric (ab):symmetric (bb) dimers. The results in Table II show that this is not the case: only when the molar ratio acetic anhydride/total fluorinated iodides is kept constant during the reaction at a slight molar excess (20–25 mole %) of Ac_2O the heterodimerization yield reaches the statistical value (50%) or even more. With a twofold Ac_2O excess, the cross-dimer yield becomes negligible. Hence, for a successful cross-dimerization the rate of acetic anhydride addition (see Experimental) has to be adjusted to the rate of iodide addition and conversion. Evidence that this methodology significantly improves the selectivities of the cross-dimer is seen by comparing the results obtained in Table III with previous literature values¹¹ for the same cross-dimerization. Previous literature work in fact reports cross-dimer selectivities <30%.

The Zn concentration does not seem to affect the selectivity of the heterodimer with respect to the homodimer: as for the homodimerization, a 20% molar excess of zinc relative to iodides added was employed.

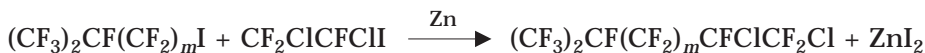
The effect of temperature on the heterodimerization is clear: as it increases, the reduction to $-\text{CF}_2\text{H}$ increases at the expense of the heterodimerization yield.

TABLE II
Yields (in %) of heterodimerizations as a function of temperature and Ac_2O concentration

| T_{R} °C | Total $\text{R}^1\text{:Ac}_2\text{O}$ | 1 | 2 | 3 | 4 | 5 |
|----------------------|---|--------|----|----|----|----|
| 40 | 1:1.2 | 60 | 17 | 18 | 3 | 2 |
| 50 | 1:1.2 | 55 | 15 | 20 | 5 | 5 |
| 60 | 1:1.2 | 4 | 31 | 31 | 17 | 17 |
| 40 | 1:2 | traces | 47 | 47 | 3 | 3 |
| 50 | 1:2 | traces | 45 | 45 | 5 | 5 |
| 60 | 1:2 | traces | 35 | 35 | 15 | 15 |

$\text{R}^1-\text{CF}_2\text{I} + \text{R}^2-\text{CF}_2\text{I} \rightarrow \text{R}^1-\text{CF}_2\text{CF}_2\text{R}^2$ (1), $\text{R}^1-\text{CF}_2\text{CF}_2\text{R}^1$ (2), $\text{R}^2-\text{CF}_2\text{CF}_2\text{R}^2$ (3), $\text{R}^1-\text{CF}_2\text{H}$ (4) and $\text{R}^2-\text{CF}_2\text{H}$ (5), where $\text{R}^1 = \text{ClCF}_2\text{CFClO}-$, $\text{R}^2 = \text{ClCF}_2\text{CFCl}-$.

The cross-dimerization of fluoroalkyl iodides having different structures such as $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_m\text{I}$ ($m = 0, 2$) and $\text{CF}_2\text{ClCFClI}$ is less efficient compared with the reaction between similar iodides. Nevertheless, a higher yield has been obtained following the experimental conditions described earlier: a constant 20% molar excess of Ac_2O relative to the total amount of fluorinated iodides during the reaction and a low temperature (40 °C). The other co-solvent was changed for solubility reasons: 1,1,1-trichloroethane was used instead of dichloromethane (see Experimental).



One of the syntheses of perfluorostyrene, a particularly stable aromatic perfluorovinyl compound¹²⁻¹⁵ is based on a copper mediated cross coupling reaction. The synthetic pathway is shown in Scheme 2.



SCHEME 2

Operating with a twofold excess of $\text{BrCF}=\text{CF}_2$ relative to $\text{C}_6\text{F}_5\text{I}$, the reaction gave a 60–65 mole % yield of the desired styrene as is shown in Table IV. The other products were the respective homodimers: perfluorobiphenyl (30–35 mole %) and perfluoro-1,3-butadiene (0–10 mole %). The

TABLE III
Yields (in %) of heterodimerization as a function of temperature and Ac_2O concentration

| T_{R} °C | $\text{R}^1\text{:Ac}_2\text{O}$ | $\text{R}^3\text{-R}^4$ | $\text{R}^3\text{-R}^3$ | $\text{R}^4\text{-R}^4$ | $\text{R}^3\text{-H} + \text{CTFE}$ |
|----------------------|----------------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------|
| 40 | 1:1.2 | 40 | 27 | 28 | 5 |
| 50 | 1:1.2 | 30 | 31 | 32 | 7 |
| 60 | 1:1.2 | traces | 37 | 38 | 25 |
| 40 | 1:2 | traces | 47 | 47 | 6 |
| 50 | 1:2 | traces | 45 | 45 | 10 |
| 60 | 1:2 | traces | 35 | 40 | 25 |

$\text{R}^3 = (\text{CF}_3)_2\text{CF}-$, $\text{R}^4 = \text{ClCF}_2\text{CFCl}-$, $\text{CTFE} = \text{ClCF}=\text{CF}_2$.

key feature of the reaction is a different reactivity of the starting materials toward copper powder: $C_6F_5I > CF_2=CFBr$. Therefore, the organocopper C_6F_5CuI is formed first and subsequently quenched by bromotrifluoroethene to obtain perfluorostyrene as the major product. If the reaction is performed with a twofold molar excess of the more reactive $ICF=CF_2$, the yield of perfluorobutadiene increases to 37 mole % with a parallel decrease in the yield of perfluorostyrene. Using a stoichiometric amount of trifluoroiodoethene the reaction proceeds giving roughly the statistical 1:2:1 distribution of the dimers and suggesting that the reactivities of C_6F_5-I and $CF_2=CF-I$ are very similar.

TABLE IV
Yields (in %) of perfluorostyrene by Cu-mediated heterodimerization

| X-CF=CF ₂ (mol. ratio) | X | C ₆ F ₅ CF=CF ₂ | C ₆ F ₅ -C ₆ F ₅ | CF ₂ =CFCF=CF ₂ |
|--------------------------------------|----|--|--|---------------------------------------|
| 2 | Br | 60 | 30 | 10 |
| 2 | I | 30 | 33 | 37 |
| 1 | I | 50 | 25 | 25 |

CONCLUSIONS

We have demonstrated that the Zn/Ac₂O mediated dimerization reaction of fluoroalkyl iodides can be directed to homo- or heterodimerization products by controlling the concentration of acetic anhydride and reaction temperature. By choosing the appropriate fluorinated alkyl iodides, the precursors of terminal perfluorinated alkenes and symmetrical or unsymmetrical dienes can be obtained.

EXPERIMENTAL

General

All ¹⁹F NMR spectra (δ, ppm; J, Hz) were recorded on a Varian Mercury 300 MHz spectrometer using CCl₃F as the internal standard. FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR ESP interfaced with OMNIC software. Gas chromatographic analyses were performed on a Carlo Erba GC 8000 Top gas chromatographer using a wide-bore 25 m column with a 0.54 μm silicon layer.

Zn powder was activated prior to use by first washing several times with acetone and then drying in a vacuum oven at 150 °C for 4 h.

The iodides $\text{ClCF}_2\text{CFCl-I}$, $\text{ClCF}_2\text{CFCl-(CF}_2)_4\text{-I}$, $\text{ClCF}_2\text{CFCIO-(CF}_2)_4\text{-I}$, $(\text{CF}_3)_2\text{CF(CF}_2)_2\text{-I}$, $\text{CF}_2=\text{CFI}$ were prepared following literature procedures¹⁶⁻¹⁹. The iodides $(\text{CF}_3)_2\text{CFI}$ and $\text{C}_6\text{F}_5\text{I}$ were purchased from Aldrich Chemical Co., bromotrifluoroethene was purchased from Matheson Ltd. They were used without further purification.

Upon request, GC-MS spectra can be furnished for the compounds synthesized and discussed in the text.

The following general dimerization procedures are modified versions of radical dimerizations already described in the literature^{4,5}.

Fluoroalkyl Iodide Homodimerization. General Procedure

The reaction is carried out in a glass round-bottom vessel in an inert atmosphere. Fluorinated alkyl iodide $\text{R}_f\text{-I}$ (10 mmol) is dissolved in 5 ml of dry CH_2Cl_2 and placed in an addition funnel; acetic anhydride (20 mmol) is dissolved in 20 ml of CH_2Cl_2 and the mixture is added to 12 mmol of Zn powder. The Zn suspension is heated to 40 °C with vigorous stirring followed by rapid addition of the iodide. A white precipitate (ZnI_2) is formed after iodide addition. The reaction is monitored both by GC and ¹⁹F NMR (disappearance of $-\text{CF}_2\text{I}$ with a concomitant appearance of a new $-\text{CF}_2-$ peak) and it is complete at 40 °C after 3 h. Vacuum distillation of the crude reaction mixture and two extractions of the organic distillate with a 10% NaOH aqueous solution followed by drying the organic solution over anhydrous MgSO_4 gave the symmetric dimer.

$\text{ClCF}_2\text{CFCIO(CF}_2)_8\text{OCFCICFCI}$ (**1**)²⁰. The corresponding dimer **1** (3.46 g, 4.70 mmol) was obtained from $\text{ClCF}_2\text{CFCIO(CF}_2)_4\text{I}$ (4.9 g, 10 mmol) according to General procedure. B.p. 270 °C; yield 95 mole %. ¹⁹F NMR (CFCl_3) of $\text{ClCF}_2\text{CFCIO-CF}_2(^1\text{CF}_2^2\text{CF}_2^3\text{CF}_2)_2\text{CF}_2\text{-OCFCICFCI}$: -68.3 dq, ²J_{FF} = 165, ³J_{FF} = ⁵J_{FF} = 11 (2 F, first signal of ClCF_2-); -69.2 dq, ²J_{FF} = 165, ³J_{FF} = ⁵J_{FF} = 13 (2 F, second signal of ClCF_2-); -74.9 m (2 F, $-\text{CFCl-O}$); -81.1 m (4 F, $-\text{OCF}_2-$); -119.0 s (4 F, $^{-1}\text{CF}_2-$); -123.1 s (4 F, $^{-2}\text{CF}_2-$); -125.5 s (4 F, $^{-3}\text{CF}_2-$).

$\text{ClCF}_2\text{CFCl(CF}_2)_8\text{CFClCFCI}_2\text{Cl}$ (**2**)²¹. The corresponding dimer **2** (3.06 g, 4.34 mmol) was obtained from $\text{ClCF}_2\text{CFCl(CF}_2)_4\text{I}$ (4.78 g, 10 mmol) according to General procedure. B.p. 290 °C; yield 87 mole %. ¹⁹F NMR (CFCl_3) of $\text{ClCF}_2\text{CFCl}(^1\text{CF}_2^2\text{CF}_2^3\text{CF}_2^4\text{CF}_2)_2\text{CFClCFCI}_2\text{Cl}$: -65.2 dq, ²J_{FF} = 171, ³J_{FF} = ⁴J_{FF} = 9 (2 F, first signal of ClCF_2-); -65.9 dq, ²J_{FF} = 167, ³J_{FF} = ⁴J_{FF} = 13 (2 F, second signal of ClCF_2-); -116.0 m (8 F, $^{-1}\text{CF}_2-$, $^{-4}\text{CF}_2-$); -123.1 m (8 F, $^{-2}\text{CF}_2-$, $^{-3}\text{CF}_2-$); -133.5 dt, ³J_{FF} = 10, ³J_{FF} = 13 (2 F, $-\text{CFCl}$).

Fluoroalkyl Iodide Heterodimerizations. General Procedure

In the same reactor as above two different (per)fluorinated alkyl iodides $\text{R}_1\text{-I}$ (5 mmol) and $\text{R}_2\text{-I}$ (5 mmol) are dissolved in 5 ml of dry CH_2Cl_2 and placed in addition funnel 1. Twelve mmol of acetic anhydride are dissolved in 10 ml of CH_2Cl_2 and are placed in addition funnel 2. Zn (12 mmol) suspended in 20 ml of CH_2Cl_2 is placed in the reaction vessel. The Zn suspension is heated to 40 °C with vigorous stirring followed by slow, simultaneous addition of the iodides (addition funnel 1) and acetic anhydride (addition funnel 2). After 3 h, a white precipitate (ZnI_2) starts to form. The reaction is monitored both by GC and ¹⁹F NMR as above and it is complete after 10 h of stirring at 40 °C. Vacuum distillation of the crude reaction mixture and two extractions of the organic distillate with a 10% NaOH aqueous solution followed by drying the organic solution over anhydrous MgSO_4 gave the cross-dimer along with the symmetric dimers and the reduced alkane.

$\text{ClCF}_2\text{CFCICF}_2(\text{CF}_2\text{CF}_2\text{CF}_2)_3\text{CF}_2\text{OCFCICF}_2\text{Cl}$ (**3**). A mixture (4.6 g) composed of the dimers **1–3**, with the following selectivities: 67% **3**, 11% **1**, 22% **2**, was obtained from $\text{ClCF}_2\text{CFCIO}(\text{CF}_2)_4\text{I}$ (2.47 g, 5 mmol) and $\text{ClCF}_2\text{CFCI}(\text{CF}_2)_4\text{I}$ (2.39 g, 5 mmol) according to General procedure. ^{19}F NMR (CFCl_3) of $\text{ClCF}_2\text{CFCI}^a\text{CF}_2^b(\text{CF}_2^c\text{CF}_2^d\text{CF}_2^e\text{CF}_2^f)_3\text{CF}_2\text{OCFCICF}_2\text{Cl}$: -64.9 dq, $^2J_{\text{FF}} = 165$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$ (1 F, first signal of $\text{ClCF}_2\text{CFCI-CF}_2^-$); -69.2 dq, $^2J_{\text{FF}} = 165$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 13$ (2 F, second signal of $\text{ClCF}_2\text{CFCI-CF}_2^-$); -71.9 dq, $^2J_{\text{FF}} = 171$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 9$ (1 F, first signal of $\text{ClCF}_2\text{CFCIO}^-$); -72.7 dq, $^2J_{\text{FF}} = 167$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 12$ (2 F, second signal of $\text{ClCF}_2\text{CFCIO}^-$); -78.2 m (1 F, $\text{ClCF}_2\text{CFCIO}^-$); -85.5 m (2 F, $\text{-CF}_2\text{O}^-$); -108.5 s (2 F, $^a\text{-CF}_2^-$); -116.3 s (2 F, $^b\text{-CF}_2^-$); -123.8 s (2 F, $^c\text{-CF}_2^-$); -126.6 s (2 F, $^d\text{-CF}_2^-$); -131.8 dt, $^3J_{\text{FF}} = 9$, $^3J_{\text{FF}} = 12$ (1 F, $\text{ClCF}_2\text{CFCI-CF}_2^-$).

$(\text{CF}_3)_2\text{CF}(\text{CF}_2\text{CF}_2)_m\text{CFCICF}_2\text{Cl}$, $m = 0$ (**4**) and $m = 1$ (**5**). This and subsequent syntheses are slightly different from all of the other dimerizations discussed: CH_2Cl_2 is substituted, for solubility reasons, with 1,1,1-trichloroethane.

$(\text{CF}_3)_2\text{CFCFCICF}_2\text{Cl}$ (**4**). Perfluoroisopropyl iodide (2.36 g, 8 mmol) and $\text{ICFClCF}_2\text{Cl}$ (3.33 g, 12 mmol) were added to 10 ml of 1,1,1-trichloroethane and the mixture was placed in dropping funnel 1. Acetic anhydride (25 mmol) diluted with 10 ml of 1,1,1-trichloroethane was placed in dropping funnel 2. In a round-bottom flask, 24 mmol of activated powdered Zn were suspended in 10 ml of 1,1,1-trichloroethane. The Zn suspension was heated to 40 °C with vigorous stirring and then the solution of both addition funnels was added to the Zn suspension over a period of 6 h. Care should be taken to avoid an excess of $\text{ICFClCF}_2\text{Cl}$ in the Zn slurry to minimize its decomposition to CTFE, as well as its dimerization. The cross-coupled product, $(\text{CF}_3)_2\text{CFCFCICF}_2\text{Cl}$, was purified by distillation to afford 1.03 g of pure material. B.p. 80 °C; yield 40%. ^{19}F NMR (CFCl_3): -65.7 dq, $^2J_{\text{FF}} = 169$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 13$ (1 F, first signal of ClCF_2^-); -66.5 dt, $^2J_{\text{FF}} = 169$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$ (1 F, second signal of ClCF_2^-); -74.5 d (6 F, CF_3^-); -133.0 dt, $^3J_{\text{FF}} = 9$, 12 (1 F, -CFCl^-); -187.7 m (1 F, -CF^-).

$(\text{CF}_3)_2\text{CF}^1\text{CF}_2^2\text{CF}_2\text{CFCICF}_2\text{Cl}$ (**5**). Before performing the dimerization reaction, $\text{ICFClCF}_2\text{Cl}$ (5 g, 18 mmol) was first telomerized¹⁷ with C_2F_4 , then $\text{ICF}_2\text{CF}_2\text{CFCICF}_2\text{Cl}$ (4.53 g, 12 mmol) was cross-dimerized with perfluoroisopropyl iodide (2.36 g, 8 mmol) as described above. After distillation, $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_2\text{CFCICF}_2\text{Cl}$ (2.43 g) was obtained. B.p. 105 °C; yield 71%. ^{19}F NMR (CFCl_3): -63.9 dq, $^2J_{\text{FF}} = 171$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$ (1 F, first signal of ClCF_2^-); -67.7 dq, $^2J_{\text{FF}} = 169$, $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$ (1 F, second signal of ClCF_2^-); -74.1 d (6 F, CF_3^-); -116.0 s (2 F, $^1\text{-CF}_2^-$); -122.3 s (2 F, $^2\text{-CF}_2^-$); -131.0 dt, $^3J_{\text{FF}} = 9$, $^3J_{\text{FF}} = 12$ (1 F, -CFCl^-); -189.0 m (1 F, -CF^-).

Dechlorination of Dimers. General Procedure

Activated powdered Zn (12 mmol), suspended in 20 ml of isopropyl alcohol (IPA), was placed in a round-bottom flask equipped with a magnetic stirrer, thermometer, reflux condenser and an addition funnel. The suspension was heated to 70–75 °C while stirring. Once the reaction temperature was reached, 10 mmol of the chlorinated dimer, previously diluted in 5 ml of IPA, was added from the addition funnel. The dechlorination began after ca. 20% of the chlorinated dimer had been added and proceeded smoothly to full conversion. A temperature increase of 5–10 °C of was observed. The conversion was monitored by NMR. Once complete conversion was achieved, the crude mixture was cooled and ZnCl_2 was filtered off. If the alkene formed was high-boiling, the IPA mixture was washed with distilled H_2O and the alkene that separated from the H_2O layer was isolated and dried over anhydrous MgSO_4 . However, if the alkene was low-boiling, the IPA solution was distilled.

$CF_2=CFO-(CF_2)_8-OCF=CF_2$ (**6**)²⁰. Compound **6** (2.06 g) was obtained from compound **1** (3.5 g, 4.76 mmol) according to General procedure. B.p. 190 °C; yield 73%. FT-IR (KBr; cm^{-1}): 1830 s ($CF_2=CFO-$); 1250–1105 s (CF). ¹⁹F NMR ($CFCl_3$) of ${}^aCF_2={}^bCFO-{}^cCF_2-$ (${}^1CF_2{}^2CF_2{}^3CF_2$)₂- ${}^cCF_2-O{}^bCF={}^aCF_2$: -82.5 m (4 F, c); -111.3 dd, ${}^2J_{FF} = 80$, ${}^3J_{FF} = 65$ (2 F, *cis*-a); -119.5 ddt, ${}^2J_{FF} = 84$, ${}^3J_{FF} = 110$ (2 F, *trans*-a); -120.0 s (4 F, ${}^{-1}CF_2$); -121.2 s (4 F, ${}^{-2}CF_2$); -123.2 s (4 F, ${}^{-3}CF_2$); -134.0 ddt, ${}^3J_{FF} = 65$, 111, ${}^4J_{FF} = 6$ (2 F, b).

$CF_2=CF-(CF_2)_8-CF=CF_2$ (**7**)²¹. Compound **7** (1.85 g) was obtained from compound **2** (4.0 g, 5.68 mmol) according to General procedure. B.p. 210 °C; yield 58%. FT-IR (KBr, cm^{-1}): 1790 s ($CF_2=CF-CF_2-$); 1250–1100 s (CF). ¹⁹F NMR ($CFCl_3$) of ${}^aCF_2={}^bCF-({}^1CF_2{}^2CF_2{}^3CF_2{}^4CF_2)_2-$ ${}^bCF={}^aCF_2$: -89.0 dd, ${}^2J_{FF} = 80$, ${}^3J_{FF} = 65$ (2 F, *cis*-a); -106.5 ddt, ${}^2J_{FF} = 84$, ${}^3J_{FF} = 110$ (2 F, *trans*-a); -120.0 s (4 F, ${}^{-1}CF_2$); -121.2 s (4 F, ${}^{-2}CF_2$); -123.2 s (4 F, ${}^{-3}CF_2$); -190.5 m (2 F, b).

$CF_2=CF-(CF_2)_8-OCF=CF_2$ (**8**). Compound **8** (2.2 g, 3.84 mmol) was obtained from the crude mixture composed of **1–3** (4.6 g, 6.4 mmol) according to General procedure followed by fractional distillation, as described above. B.p. 200 °C; yield 60%. FT-IR (KBr, cm^{-1}): 1838 s ($CF_2=CFO-$); 1786 s ($CF_2=CF-CF_2-$). ¹⁹F NMR ($CFCl_3$) of ${}^aCF_2={}^bCF{}^cCF_2-$ (${}^1CF_2{}^2CF_2{}^3CF_2$)₃- ${}^dCF_2-O{}^eCF={}^fCF_2$: -91.5 m (2 F, d); -92.0 dd, ${}^2J_{FF} = 80$, ${}^3J_{FF} = 65$ (1 F, *cis*-a); -108.3 ddt, ${}^2J_{FF} = 84$, ${}^3J_{FF} = 110$ (1 F, *trans*-a); -113.5 dd, ${}^2J_{FF} = 80$, ${}^3J_{FF} = 65$ (1 F, *cis*-f); -122.5 ddt, ${}^2J_{FF} = 84$, ${}^3J_{FF} = 110$ (1 F, *trans*-f); -121 s (2 F, c); -123.5 s (2 F, ${}^{-1}CF_2$); -125.5 s (2 F, ${}^{-2}CF_2$); -126.3 s (2 F, ${}^{-3}CF_2$); -136.3 ddt, ${}^3J_{FF} = 65$, 111, ${}^4J_{FF} = 6$ (2 F, e); -189.5 m (1 F, b).

$(CF_3)_2CFCF=CF_2$ (**9**). Compound **9** (0.47 g, 1.87 mmol) was obtained from compound **4** (1 g, 3.1 mmol) according to General procedure. B.p. 30 °C; yield 60%. FT-IR (KBr, cm^{-1}): 1786 s ($CF_2=CF-CF-$); 1210–1150 s (CF). ¹⁹F NMR ($CFCl_3$): -72.3 d (6 F, CF_3); -86.2 dd, ${}^2J_{FF} = 82$, ${}^3J_{FF} = 63$ (1 F, *cis*= CF_2); -106.5 ddt, ${}^2J_{FF} = 83$, ${}^3J_{FF} = 112$ (1 F, *trans*= CF_2); -186.8 m (1 F, -CF); -192.7 m (1 F, =CF-).

$(CF_3)_2CFCF_2CF_2CF=CF_2$ (**10**). Compound **10** (1.83 g, 5.24 mmol) was obtained from compound **5** (2.4 g, 5.7 mmol) according to General procedure. B.p. 65 °C; yield 92%. FT-IR (KBr, cm^{-1}): 1786 s ($CF_2=CF-CF-$); 1210–1150 s (CF). ¹⁹F NMR ($CFCl_3$) of $(CF_3)_2CF{}^1CF_2{}^2CF_2CF=CF_2$: -74.3 d (6 F, CF_3); -89.4 dd, ${}^2J_{FF} = 80$, ${}^3J_{FF} = 65$ (1 F, *cis*= CF_2); -106.5 ddt, ${}^2J_{FF} = 84$, ${}^3J_{FF} = 110$ (1 F, *trans*= CF_2); -120.0 s (2 F, ${}^{-1}CF_2$); -121.2 s (2 F, ${}^{-2}CF_2$); -188.5 m (1 F, -CF); -191.4 m (1 F, =CF-).

$C_6F_5CF=CF_2$ (**11**). The reaction was carried out in a stainless-steel vessel equipped with a pressure gauge. C_6F_5I (2.39 g, 10 mmol) and $BrCF=CF_2$ (3.22 g, 20 mmol) were dissolved in 50 ml of anhydrous dimethylacetamide (DMA) and siphoned into the evacuated vessel which contained 20 mmol of Cu powder. The slurry was heated to 120 °C for 5 h. GC analysis of the crude reaction mixture showed the following product distribution: 65% $C_6F_5CF=CF_2$, 33% perfluorobiphenyl and 2% perfluorobutadiene. The mixture was fractionally distilled and the target compound **11** (1.4 g, 5.7 mmol) was obtained. B.p. 126 °C; yield 57%. The spectroscopic data match those reported in the literature^{13,22,23}.

Special thanks go to Prof. J. Kvičala for helpful discussions regarding both the manuscript and interpretation of ¹⁹F NMR spectra.

REFERENCES

- Lowry T. L., Richardson K. S.: *Mechanism and Theory in Organic Chemistry*, p. 146. Harper and Row, New York 1981.

2. Henne A. L.: *J. Am. Chem. Soc.* **1953**, *75*, 5750.
3. Chen G. J., Tamborski C.: *J. Fluorine Chem.* **1987**, *36*, 123.
4. Gorbunova T. I., Zapevalov A. Ya., Saloutin V. I.: *Russ. J. Org. Chem.* **1999**, *35*, 1557.
5. Fearn J. E.: *J. Res. Nat. Bureau Stds.* **1971**, *75A*, 41.
6. a) Babb D. in: *Fluoropolymers 1: Synthesis* (Hougham et al., Eds), pp. 25–50. Plenum Press, New York 1999; b) Takayuki A., Tetsuo S., Takafumi Y., Masahiro K. (Daikin Industries Ltd.): U.S. 5,670,593 (1997); *Chem. Abstr.* **1997**, *124*, 177249.
7. Buttafava A., Guarda P. A., Marchionni G., Ronconi R., Fautitano A.: *J. Fluorine Chem.* **2002**, *114*, 9.
8. Folest J. C., Nedelec J. Y., Perichon J.: *J. Chem. Res., Synop.* **1989**, 394.
9. Ginah F. O., Donovan T. A., Suchan S. D., Pfennig D. R., Ebert J. W.: *J. Org. Chem.* **1990**, *55*, 584.
10. Wlassics I., Tortelli V.: *J. Fluorine Chem.* **2008**, *129*, 359.
11. Knunyants I. L., Shokina V. V.: *Dokl. Akad. Nauk SSSR* **1959**, *129*, 328.
12. Wall L. A., Brow D. W.: *J. Fluorine Chem.* **1972**, *2*, 73.
13. Soloski E. J., Ward W. E., Tamborski C.: *J. Fluorine Chem.* **1972**, *2*, 361.
14. Tamborski C., Moore G. J.: *J. Fluorine Chem.* **1971**, *26*, 153.
15. DePasquale R. J., Tamborski C.: *J. Org. Chem.* **1969**, *34*, 1736.
16. Pedersen S. D., Qiu W., Qiu Z.-M., Kotov S. V., Burton D. J.: *J. Org. Chem.* **1995**, *61*, 8024.
17. Wlassics I., Tortelli V.: *J. Fluorine Chem.* **2006**, *127*, 240.
18. Améduri B., Boutevin B., Kostov G. K., Petrova P.: *J. Fluorine Chem.* **1995**, *74*, 261.
19. Hansen S. W., Spawn T. D., Burton D. J.: *J. Fluorine Chem.* **1987**, *35*, 415.
20. Tortelli V., Millesanti S., Calini P. (Ausimont): Japan 213256 (2005).
21. Knunyants I. L., Li C.-Y., Shokina V. V.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1961**, 1462.
22. Callander D. D., Coe P. L., Matough M. F. S., Mooney E. F., Uff A. J., Winson P. H.: *Chem. Commun.* **1966**, *22*, 820.
23. Tamborski C., Soloski E. J., DePasquale R. J.: *J. Organomet. Chem.* **1968**, *15*, 494.