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IONIC TELOMERIZATION OF CHLOROFLUOROPROPIONYL FLUORIDES WITH HEXAFLUOROPROPENE OXIDE

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SUMMARY

Six chlorofluoropropionyl fluorides were synthesized by converting a $-CCl_3$ group in perhalogenated chlorofluoropropanes to a -COF group in two reaction steps. The ionic telomerization of the acyl fluorides with hexafluoropropene oxide, catalyzed by fluoride ion, afforded mainly a mixture of 1:1 to 1:3 telomers. In some cases, substitution of chlorine for fluorine in the acyl moiety and hexafluoropropene oxide oligomerization occurred as side reactions. The effect of the number of chlorines in the starting acyl fluoride on the telomer distributions and by product formation is discussed. The reactivity order of the acyl fluorides Y-COF in the telomerization reaction was: CF_3-CClF (2a), $CClF_2$-CF_2 (2b) > CF_3-CCl_2 (3a), $CClF_2$-CClF (3b) > $CClF_2$-CCl_2 (4a), CCl_2F-CClF (4b). Possible reaction pathways are discussed.

INTRODUCTION

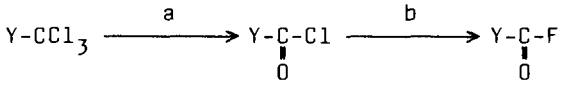
Fluorinated polyethers are widely used in engineering as lubricants and in chemistry as precursors for fluorinated monomers [1]. The best method for their preparation is the ionic telomerization of fluorinated acyl fluorides with hexafluoropropene oxide, catalyzed by fluoride ion. The product composition (i.e. telomer distribution) and yields of products are strongly influenced by the nature of the fluoride ion

0022-1139/90/$3 50

source and solvent used, caesium fluoride and tetraethylene glycol dimethyl ether being the most effective system [2,3]. The influence of the starting perfluoroacyl fluoride structure on the course of the telomerization, with respect to the acyl fluoride chain length and bulkiness, was also studied [4]. In contrast to perfluorinated acyl fluorides, the ionic telomerizations of halogenofluoroacyl fluorides, viz. trichloroacetyl fluoride [5], dichlorofluoroacetyl fluoride [1], and 2,3-dichlorotrifluoropropionyl fluoride [6], yielded substantially lower amounts of the corresponding telomers. However, detailed information concerning these reactions has not been published and we now report our results of the ionic telomerizations of perhalogenated chlorofluoropropionyl fluorides with hexafluoropropene oxide.

RESULTS AND DISCUSSION

We developed a new synthetic route for the synthesis of chlorofluoropropionyl fluorides, which is based on a two-step transformation of a trichloromethyl group to a fluorocarbonyl group (Scheme 1). Syntheses of the starting chlorofluoropropanes were described formerly [7-9]: some were isomeric mixtures, whose content was determined by ^{19}F NMR spectroscopy [10]. Isomers not possessing a $-CCl_3$ group were separated chemically in the stage of acyl chloride formation; the isomeric halogenopropanes with a $-CCl_3$ group were transformed to the corresponding acyl fluorides together with the main



Y = CF_3-CClF	2a	Y = $CClF_2$-CCl_2	4a
$CClF_2$-CF_2	2b	CCl_2F-CClF	4b
CF_3-CCl_2	3a	a oleum [7]	
$CClF_2$-CClF	3b	b KF/MeCN [11]	

Scheme 1.

isomers and their content was also determined by ^{19}F NMR spectroscopy.

For the ionic telomerizations, caesium fluoride and tetraethylene glycol dimethyl ether were used as the most efficient catalytic system minimizing hexafluoropropene oxide (1, HFPO) oligomerization. Non-pressure reaction conditions were preferred, allowing monitoring of the reaction mixture composition by GLC. For the same reason, gaseous epoxide 1 was continuously added to the reaction mixture and its concentration was maintained at a relatively low level. This experimental arrangement supported chain transfer to the telogenic acyl fluorides 2-4 and resulted in formation of telomers of a low telomerization degree (Scheme 2, path I). Addition of 1 was stopped when the required telomer ratio was achieved or, for acyl fluorides 4a,4b, when reaction ceased. The compositions of the reaction mixtures at the end of the reactions are shown in Table 1.

TABLE 1

The reaction mixture composition of the telomerization reactions[a]

Acyl fluoride		Composition (%)					
		AF[b]	Telomers				By-products
			1:1	1:2	1:3	1:4	
2a	CF_3-CClF-COF	1	38	48	11	1	1
2b	$CClF_2$-CF_2-COF	1	46	45	7	0	1
3a	CF_3-CCl_2-COF	14	29	26	15	5	1
3b	$CClF_2$-CClF-COF	12	21	30	31	3	3
4a	$CClF_2$-CCl_2-COF	39	20	15	9	0	17
4b	CCl_2F-CClF-COF	49	6	5	2	0	38

[a] For reaction conditions see Experimental;

[b] Starting acyl fluoride.

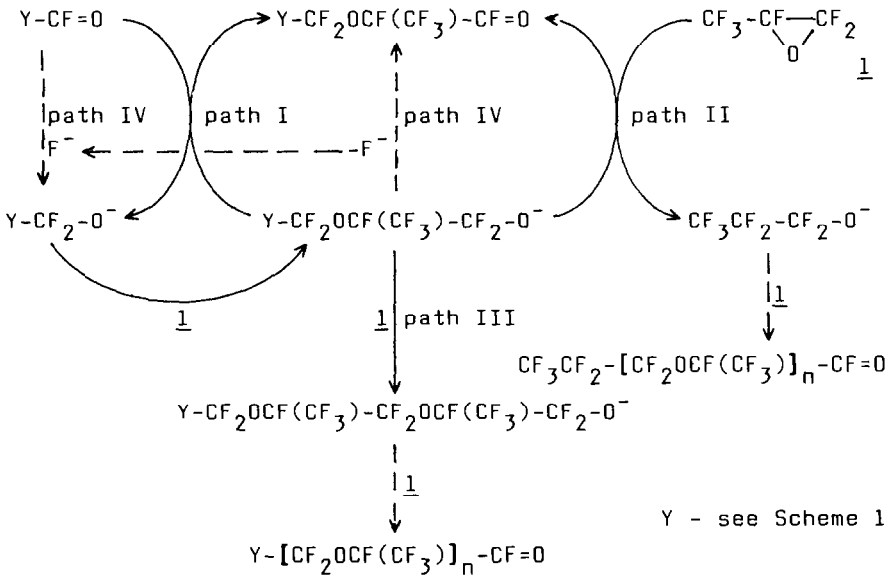
Monochloroacyl fluorides 2a,2b afforded, at nearly total conversion mainly 1:1 and 1:2 telomers (5,6). Dichlorotrifluoropropionyl fluorides 3a,3b gave higher telomers even at a lower conversion of the starting acyl fluorides; under the total conversion of acyl fluoride 3b the mixture of telomers contained three HFPO units on average, i.e. higher telomers predominated. These results show the reactivity order of acyl fluorides in the ionic telomerization to be:

C_2ClF_4-COF > $C_2Cl_2F_3$-COF > $C_2Cl_3F_2$-COF

2a,2b 3a,3b 4a,4b

Oligomerization of HFPO, induced by caesium fluoride with an HFPO trimer, yielded HFPO dimer in addition to higher oligomers [12]. The formation of the HFPO dimer was explained by a chain transfer from oligomer alkoxide to HFPO [12]. Possible transformation paths of 1:1 telomer in our reaction system are depicted in Scheme 2. On the basis of the above assumption [12] we suppose that the chain transfer from telomeric alkoxides to the starting acyl fluoride could be the main factor influencing the relative distribution of telomers (path I, Scheme 2), as the other reaction paths, namely chain transfer to epoxide 1 (path II in Scheme 2) and chain propagation (path III in Scheme 2) are reactions proceeding at approximately the same rate for all the acyl fluorides. The transfer of the reaction centre from a telomeric alkoxide via fluoride ion abstraction and its reaction with acyl fluoride (path IV in Scheme 2) has been reported to be improbable [13].

Nearly equal distribution of telomers in the reaction of isomeric acyl fluorides (e.g. 2a and 2b, Table 1) indicates that both α- and β-chlorine substituents in the starting acyl fluoride influence the reactivity in the same manner. When comparing the telomerizations of acyl fluorides 2 and 3, a higher average telomerization degree was achieved with 3 as a consequence of enhancing path III participation (e.g. chain propagation). In contrast, by using an acyl fluoride of high reactivity, e.g. fluorosulfonyldifluoroacetyl fluoride, for the telomerization, preferential involvement of path I resulted



Scheme 2.

in formation of the corresponding 1:1 telomer in a high yield (ca. 90%) even at the total conversion of the starting acyl fluoride [14]. When a less active catalytic system (KF in acetonitrile [15]) was used, or higher reaction temperatures (aiming to suppress the chain propagation), only small changes in the telomer distribution were observed, whereas greater portions of HFPO oligomers as byproducts were formed by path II participation [14]. Thus, the reactivity of the starting acyl fluoride proved to be the main factor influencing path I participation in the telomerization system and thence the telomer distribution. In our opinion, the low yields of 1:1 telomers of chlorinated acyl fluorides reported [1,5,6] arose from failure to suppress chain propagation at sufficient acyl fluoride conversion.

The telomerizations of unreactive trichlorodifluoropropionyl fluorides 4a,4b were characterized by two features: first, the reaction ceased after a period, second, the composition of the resulting reaction mixture appeared to be very complex. Neither rectification, nor preparative GLC

yielded individual products of sufficient purity, and therefore rectification fractions were subjected to the direct analyses by the ^{19}F NMR and GC-MS spectroscopy.

In reaction mixtures starting from both acyl fluorides 4a and 4b, we found three sets of polyethers by ^{19}F NMR spectroscopy: first, telomers of acyl fluorides 4a and 4b, respectively, second, oligomers of HFPO, and third, telomers containing a 2-chlorohexafluoro-1-propoxy group, probably formed by parallel fluorination and telomerization. It is interesting that neither isomeric telomers with a 3-chlorohexafluoro-1-propoxy group, nor intermediate telomers with two chlorine atoms were identified in the NMR spectra, and this observation will be subject of further work.

The GC-MS spectra confirmed the presence of three sets of telomers, i.e. fully fluorinated compounds, a set with one chlorine atom, and a set with three chlorine atoms in the molecule (Table 2). In all cases, easy fragmentation occurred, as shown in Table 2. By comparing mass spectral sets of some fractions we were able to identify the near-mass fragments as a further confirmation of the mixture-component formulae.

In the fluorination of the acyl part of the ethers, caesium fluoride, the catalyst, was consumed. Thus we conclude that the fluorination was the reason why the telomerizations were stopped after the consumption of the fluoride catalyst.

EXPERIMENTAL

The temperature data were uncorrected. GLC analyses were performed on a Chrom 41 (Laboratorní přístroje, Prague) instrument (FID, 3.8 m x 3 mm column packed with Silicone SE-301 oil (10% $^{w}/_{w}$ on Chromaton N-AW-DMCS (Lachema, Brno), grading 0.1 - 0.125 mm). Infrared spectra were recorded on a Perkin-Elmer 325 instrument, mass spectra were scanned on a JEOL DX 303/DA 5000 spectrometer (ionizing voltage 70 eV). The NMR spectra were taken on a Varian XL-100/15 (CW, ^{19}F at 94 MHz) and a Bruker 400 AM (FT, ^{19}F at 376 MHz) apparatus: $CFCl_3$ as the internal standard, chemical shifts in ppm (s singlet, d doublet, t triplet, q quadruplet, m multiplet), solvent $CDCl_3$ except fluorinated telomers, which were measured in a 1:1 diethyl ether - tetrahydrofurane-d_8 mixture.

TABLE 2

GC-MS analysis of telomers based on HFPO (1) and $CCl_2FCClFCOF$ (4b) (fraction boiling at 126-135°C/2.0 kPa)

Ret. time	8'24"	8'52"	10'12"	11'22"	12'42"	13'42"
Relative area (%)	48	59	94	48	44	33
Significant fragments: m/z, relative intensity (fragment)$^{+\cdot}$	667 0.2	683 0.5	683 0.1	645 0.3	645 0.4	645 0.3
	$C_{12}F_{25}O_3$	$C_{12}ClF_{24}O_3$	$C_{12}ClF_{24}O_3$	$C_{12}F_{23}O_4$	$C_{12}F_{23}O_4$	$C_{12}F_{23}O_4$
	501 1.5	645 0.3	645 0.3	517 0.3	549 0.2	383 0.4
	$C_9F_{19}O_2$	$C_{12}F_{23}O_4$	$C_{12}F_{23}O_4$	$C_9ClF_{18}O_2$	$C_9Cl_3F_{16}O_2$	$C_6Cl_3F_{10}O$
	479 2	517 0.3	517 0.4	217 2	217 7	217 5
	$C_9F_{17}O_3$	$C_9ClF_{18}O_2$	$C_9ClF_{18}O_2$	$C_3Cl_3F_4$	$C_3Cl_3F_4$	$C_3Cl_3F_4$
	335 10	185 21	185 18	185 13	185 4	185 3
	$C_6F_{13}O$	C_3ClF_6	C_3ClF_6	C_3ClF_6	C_3ClF_6	C_3ClF_6
	313 14	169 100	169 100	169 100	169 100	169 100
	$C_6F_{11}O_2$	C_3F_7	C_3F_7	C_3F_7	C_3F_7	C_3F_7
	169 100	135 4	135 4	101 10	101 44	101 27
	C_3F_7	C_2ClF_4	C_2ClF_4	CCl_2F	CCl_2F	CCl_2F
	119 39	85 8	85 6	85 18	85 31	85 23
	C_2F_5	$CClF_2$	$CClF_2$	$CClF_2$	$CClF_2$	$CClF_2$
	69 59	69 77	69 67	69 67	69 81	69 67
	CF_3	CF_3	CF_3	CF_3	CF_3	CF_3
Terminal group	C_3F_7O-	C_3ClF_6O-	C_3ClF_6O-	$C_3ClF_4X_2O$-	$C_3Cl_3F_4O$-	$C_3Cl_3F_4O$-

The new compounds 2,2,3-trichlorodifluoropropionyl fluoride (4a), 2,3,3-trichlorodifluoropropionyl fluoride (4b), 5-chloroheptafluoro-2-trifluoromethyl-3-oxahexanoyl fluoride (5a), 6-chloroheptafluoro-2-trifluoromethyl-3-oxahexanoyl fluoride (5b), 8-chlorodecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (6a), 9-chlorodecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (6b), 5,5-dichlorohexafluoro-2-trifluoromethyl-3-oxahexanoyl fluoride (7a), 8,8-dichlorooctafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (8a), 8,9-dichlorooctafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (8b) and 5,5,6-trichloropentafluoro-2-trifluoromethyl-3-oxahexanoyl fluoride (9a) were characterized by ^{19}F NMR spectra, IR spectra, elemental analysis, and some of them by mass spectrometry (4a,4b), but only 4a,4b,5a,5b and 6b had purities of 90% or better. Compounds 5a and 6b have two chiral centres and must be mixtures of two diastereoisomers.

Chemicals used

Anhydrous caesium fluoride (FLUKA AG) and potassium fluoride (Lachema, Brno) were finely ground in a dry atmosphere and dried 4h *in vacuo* at 160 °C. Tetraethylene glycol dimethyl ether (tetraglyme) and acetonitrile were dried over calcium hydride and distilled prior to use. Hexafluoropropene (Matheson) was used without further purification.

2-Chlorotetrafluoropropionyl chloride [8], dichlorotrifluoropropionyl chlorides and trichlorodifluoropropionyl chlorides [7] and hexafluoropropene oxide [1,16] were made by standard routes.

1,1,1,3-Tetrachlorotetrafluoropropane

A fraction from rectification ([9], b.p. 87.5-90.2 °C, 656 g, 52%wt. $C_3Cl_3F_3$, 48% $C_3HCl_3F_4$) was chlorinated in an immersion-well photochemical reactor (medium pressure mercury lamp Tesla, RVK 125) at room temperature, until 99% conversion was achieved (*ca.* 60 h). The resulting mixture (807 g, 52% $C_3Cl_5F_3$, 47% $C_3Cl_4F_4$, 1% the starting mixture) afforded 1,1,1,3-tetrachlorotetrafluoropropane (293.9 g, 1.154 mol, purity 99%), b.p. 112-116 °C (reported [17] 114 °C), isomer admixtures (^{19}F NMR [10]): 7% 1,1,3,3-tetrachloro-, 3% 1,1,1,2-tetrachlorotetrafluoropropane.

3-Chlorotetrafluoropropionyl chloride

A mixture of 1,1,1,3-tetrachlorotetrafluoropropane (144.8 g, 570 mmol; for purity see above), fuming sulphuric acid (50 ml, ca. 60% SO_3 content), mercuric oxide (1 g), and silver nitrate (0.24 g) was refluxed 8 h with stirring. Crude product was periodically distilled off via a Vigreux column to yield a fraction of b.p. 42-45°C (90.6 g). Admixture of sulphur trioxide was removed by extraction with sulphuric acid (90%, 10 ml). Final distillation afforded 3-chlorotetrafluoropropionyl chloride of b.p. 43-45°C (reported [18] 49-51°C), 71.2 g (358 mmol, 63%), purity (GLC) 98%, isomer admixture (^{19}F NMR) of 6% 2-chlorotetrafluoropropionyl chloride. ^{19}F NMR spectra: $CClF_2$-CF_2-COCl, t -69.6 ($CClF_2$-), t -112.4 (-CF_2-), ^3J 4; CF_3-CClF-COCl, d -78.8 (CF_3-), q -125.2 (-CClF-), ^3J 6.

Chlorofluoropropionyl fluorides 2a, 2b, 3a, 3b, 4a and 4b

General procedure

To a stirred mixture of acetonitrile (25-40 ml, in the case of trichlorodifluoropropionyl chlorides 2-4 ml only to minimize contamination of the resulting acyl fluorides) and potassium fluoride (1.6-4.5 molar excess with respect to acyl chloride), starting acyl chloride was dropwise added at room temperature. The reaction flask was heated 2-16 h at temperatures of c. 30°C above the product boiling point. The crude acyl fluoride was obtained by periodical distillation through a Vigreux column. Results are listed in Table 3. The purity of products was checked by GLC, the structure was verified by the ^{19}F NMR and mass spectra, which are listed in Tables 4 and 5, respectively.

Ionic telomerizations of chlorofluoropropionyl fluorides 2-4 with hexafluoropropene oxide

General procedure

Into a reaction flask, equipped with an efficient stirrer with a gas-tight shaft and low-temperature condenser, tetraethylene glycol dimethyl ether (30-90% mol. with respect to acyl fluoride) and caesium fluoride (10-20% mol.) were added under dry atmosphere. After cooling to -25°C, acyl fluoride was dropwise added, the mixture was slowly heated to room temperature, allowed to react 1 h and cooled to -25°C. Gaseous hexafluoropropene oxide (1.3-1.7 fold excess relative to acyl fluoride) was introduced into the

TABLE 3

Results of the preparation of acyl fluorides 2a, 2b, 3a, 3b, 4a and 4b

Starting compound Y-COCl				Product Y-COF				
Y	g	mmol		B.p. °C	Yield g	Yield %	Purity %	Isomer content %
CF_3-$CClF$	47.0	236	2a	12-14[a]	36.1	84	98	<0.5
$CClF_2$-CF_2	46.7	245	2b	10-13	40.6	91	98	4/2a
CF_3-CCl_2	9.0	42	3a	45-48[b]	5.8	70	90	<0.5
$CClF_2$-$CClF$	50.8	236	3b	45-50[c]	40.8	87	98	8/3a,3/3c
$CClF_2$-CCl_2	24.8	107	4a	72-74	16.9	73	93	<0.5
CCl_2F-$CClF$	54.7	248	4b	78-82.5	34.5	65	90	14/4a

[a] Reported [19] 11°C; [b] reported [20] 41°C; [c] reported [21] 49-50°C.

reaction mixture for 2-2.5 h, which was then maintained 0.5 h at -25°C, heated to room temperature and volatile components were then removed (the reactant amounts for individual telomerizations are given in Table 6). The bottom layer was separated, the remaining mixture was centrifuged and the bottom layer formed was taken off with a syringe. Collected crude products were fractionated. The yields of 1:1 and 1:2 telomers isolated are given in Table 7. Their elemental analyses and the NMR spectra are listed in Tables 8 and 9, respectively. All compounds prepared showed a strong absorption at 1800-1890 cm^{-1} in the IR spectra, confirming the presence of a -COF group in the product molecules.

Telomerization of 2,2,3-trichlorodifluoropropionyl fluoride (4a)

The crude product (11.5 g) contained (GLC at 150°C, ^{19}F NMR): 39% 4a, 44% telomers of 4a (20% 5,5,6-trichloropentafluoro-2-trifluoromethyl-3-oxa-hexanoyl fluoride (9a), 24% higher telomers), a fraction of telomers with a terminal 2-chlorohexafluoro-1-propoxy group, and oligomers of HFPO (1).

TABLE 4

^{19}F NMR spectra of chlorofluoropropionyl fluorides 2-4

Acyl fluoride		Chemical shifts[a]			Coupling constants[b]			
a b c		a	b	c	$^3J_{ab}$	$^3J_{bc}$	$^4J_{ac}$	$^2J_{aa}$
CF_3-CClF-COF	2a	t -80.1	dq -133.2	dq +21.6	7	17	7	
$CClF_2$-CF_2-COF	2b	dt -71.1	dt -117.2	quintet +26.2	6	7	7	
CF_3-CCl_2-COF	3a	d -77.2		q +20.5			9	
$CClF_2$-CClF-COF	3b	dt -64.7 dt -67.9	dt -125.7	dt +22.4	9 10	15	11	173
CCl_2F-CF_2-COF	3c	q -73.7	dd -112.2	dt +27.5	8	11	9	
$CClF_2$-CCl_2-COF	4a	d -62.4		t +22.1			12	
CCl_2F-CClF-COF	4b	t -66.7	t -118.5	t +23.3	15	15	15	

[a] In ppm upfield from $CFCl_3$ (s - singlet, d - doublet, t - triplet, q - quadruplet); [b] in Hz.

TABLE 5

Major fragments of chlorofluoropropionyl fluorides Y-COF (2-4) in the mass spectra

m/z, relative intensity, $(fragment)^{+\cdot}$					
Y (Acyl fluoride Y-COF)					
CF_3CClF	$CClF_2CF_2$	CF_3CCl_2	$CClF_2CClF$	$CClF_2CCl_2$	CCl_2FCClF
2a	2b	3a	3b	4a	4b
135 21	135 15	151 100	151 18	167 16	167 5
M - COF	M - COF	M - COF	M - COF	M - COF	M - COF
94 8	119 49	110 11	135 36	151 12	151 36
M - CF_4	M - COCl	M - CF_4	M - COCl	M - COCl	M - COCl
85 65	85 100	101 31	101 20	132 14	132 10
$CClF_2$	$CClF_2$	CCl_2F	CCl_2F	M - COClF	M - COClF
69 100	69 33	85 18	85 100	101 13	101 100
CF_3	CF_3	$CClF_2$	$CClF_2$	CCl_2F	CCl_2F
47 14	47 18	69 47	69 8	85 100	85 33
COF	COF	CF_3	CF_3	$CClF_2$	$CClF_2$
		47 18	47 16	63 20	47 20
		COF	COF	COCl	COF
				47 16	
				COF	

Telomerization of 2,3,3-trichlorodifluoropropionyl fluoride (4b)

The crude product (24.5 g) consisted of (GLC at 150 °C, ^{19}F NMR) 49% 4b, 13% telomers of acyl fluoride 4b (6% 1:1 telomer, 7% higher telomers), a fraction of telomers with a terminal 2-chlorohexafluoro-1-propoxy group and oligomers of HFPO (1), separation of which by rectification failed. The GC-MS analysis of the selected fraction is given in Table 2.

TABLE 6

Reactant amounts for the ionic telomerizations

Hexafluoropropene oxide		Acyl fluoride Y-COF			
g	mmol	Y		g	mmol
23	139	CF_3-$CClF$	2a	18.7	102
24	145	$CClF_2$-CF_2	2b	16.4	89
4.7	28	CF_3-CCl_2	3a	3.1	16
19	115	$CClF_2$-$CClF$	3b	14.9	75
10.7	65	$CClF_2$-CCl_2	4a	11.2	52
17.2	104	CCl_2F-$CClF$	4b	20.8	97

TABLE 7

Elemental analyses of telomeric acyl fluorides 5–8

Element	Compound[a] (Calculated/Found %)							
%	5a	5b	6a	6b	7a	7b	8a	8b
C	20.6 / 21.6	20.6 / 21.1	21.0 / 21.7	21.0 / 21.5	19.7 / 20.2	19.7 / 20.2	20.4 / 21.6	20.4 / 20.7
Cl	9.9 / 10.2	9.9 / 10.2	6.9 / 6.5	6.9 / 5.6	19.4 / 17.0	19.4 / 19.4	13.4 / 12.9	13.4 / 11.5
F	60.0 / 61.0	60.0 / 61.6	62.8 / 62.9	62.8 / 64.1	52.1 / 59.6	52.1 / 51.6	57.3 / 59.0	57.3 / 59.4
Purity %	94	98	86	98	78	71	72	78

[a] 5a,5b $C_6ClF_{11}O_2$; 6a,6b $C_9ClF_{17}O_3$; 7a,7b $C_6Cl_2F_{10}O_2$; 8a,8b $C_9Cl_2F_{16}O_3$.

TABLE 8

Telomeric acyl fluorides of formula Y-[$CF_2OCF(CF_3)]_nCF_2O-CF(CF_3)COF$ prepared

Product			Preparative yield				Boiling point	Purity[a]
Y	n		g	mmol	% on Y-COF	% on HFPO	°C/kPa	%
CF_3CClF	0	5a	11.6	33	32	24	78-85/100	94
	1	6a	13.4	26	25	38	138-148/100	86
$CClF_2CF_2$	0	5b	8.2	24	16	26	88-91/100	98
	1	6b	3.4	6.6	7.4	9.2	148-150/100	98
CF_3CCl_2	0	7a	1.4	3.8	25	14	110-130/100	78
	1	8a	1.4	2.6	17	19	50-75/2.4	72
$CClF_2CClF$	0	7b	2.0	5.5	7.3	4.8	119-124/100	71
	1	8b	6.1	12	15	20	50-77/1.6	78
$CClF_2CCl_2$	0	9a	0.7	1.8	3.5	3.0	28-52/2.1	51

[a] Based on GLC (100 °C, 150 °C) and ^{19}F NMR; impurities are mainly lower and higher telomers.

TABLE 9

^{19}F NMR spectra of telomeric acyl fluorides 5–9

Acyl fluoride			Y-[CF_2(a)$OCF(CF_3)$(b)(c)]$_n$$CF_2(d)O$-$CF(CF_3)(e)COF$ (f, g, h, i) Chemical shifts[j]								
Y	n		a	b	c	d[k]	e	f[l]	g	h	i
CF_3CClF (a, b)	0	5a	s -78.1	m -139.6				dm dm -75.5 -82.1	d -130.4	m -82.2	m +26.1
	1	6a	d -78.3	m -139.3	m -77.5	t -144.8	m -79.9	dm dm -78.3 -85.0	m -130.3	m -82.3	m +26.0
$CClF_2CF_2$ (a, b)	0	5b	t -68.9	s -123.9				dm dm -77.5 -84.8	d -130.6	m -82.2	m +26.1
	1	6b	q -68.9	s -123.8	m -79.4	t -145.2	m -80.1	dm dm -78.6 -85.4	t -130.7	m -82.1	m +26.3
CF_3CCl_2 (a)	0	7a	t -74.6					dm dm -72.1 -79.0	d -130.6	m -82.0	m +26.9
	1	8a	m -74.9		m -74.1	t -145.4	m -79.9	dm dm -78.8 -84.8	m -130.5	m -82.1	m +26.5
$CClF_2CClF$ (a, b)	0	7b	dm[m] dm -63.7 -64.9	m -133.0				dm dm -73.6 -80.5	t -130.6	m -82.0	m +26.4
		8b	dm dm -63.6 -64.9	m -132.7	m -75.2	t -145.3	m -79.9	dm dm -78.5 -85.1	m -130.6	m -82.0	m +26.4
$CClF_2CCl_2$ (a)	0	9a	t -59.8					dm dm -69.8 -76.6	m -130.6	q -82.2	q +26.8
CCl_2FCClF (a, b)	0	9b	m -65.4	m -126.5				dm dm -68.9 -75.7	m -130.6	m -82.0	m +26.5

[j] In ppm upfield from $CFCl_3$; [k] J ca. 20 Hz; [l] $^2J_{ff}$ ca. 145 Hz; [m] $^2J_{aa}$ ca. 174 Hz.

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