Journal of Fluorine Chemistry, 15 (1980) 353–380

Received: July 13, 1979

FLUORINATION OF 2-ALKYL-SUBSTITUTED OXANES. THE SYNTHESIS AND PURIFICATION OF PERFLUORO(2-ALKYL-SUBSTITUTED OXANE)S*

TAKASHI ABE, EIJI HAYASHI, HAJIME BABA, KAZUO KODAIRA and
SHUNJI NAGASE

Government Industrial Research Institute, Nagoya
Hirate-machi, Kita-ku, Nagoya (Japan)

SUMMARY

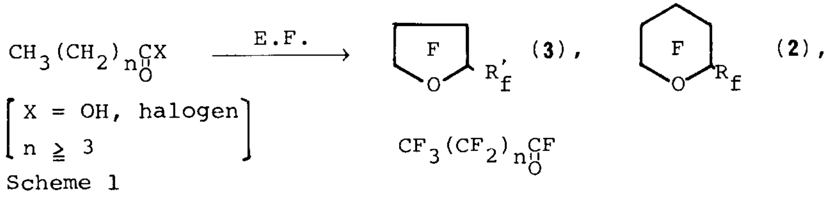
Five kinds of 2-alkyl-substituted oxanes like 2-ethyloxane, 2-n-propyloxane, 2-iso-propyloxane, 2-n-butyloxane and 2-n-amyloxane were fluorinated electrochemically to give the corresponding perfluoro(2-alkyloxane)s. The perfluoro(2-alkyloxane)s were obtained in good yields from these starting materials together with isomeric perfluoro(2-alkyloxolane)s, perfluoro(2-alkyl-5-methyloxolane)s and perfluoro(dialkyl ether)s. The purification of the perfluoro(2-alkyloxane)s which contained small amounts of isomeric perfluoro(2-alkyloxolane)s was successfully achieved by recovering the former unreacted after treating these mixture with anhydrous aluminum chloride at 150∼160 °C during ∼48 hrs in order to convert the latter into the easy-separable perfluoro-(2,5,5-trichloro-2-alkyloxolane)s. Small quantities of new perfluoro(5,5-dichloroalkanoyl chloride)s were also among the chlorination products. The spectroscopic data as well as the physical properties of these new fluorination products, and perfluoro(2,5,5-trichloro-2-alkyloxolane)s and perfluoro(5,5-dichloroalkanoyl chloride)s are presented.

---

* Presented at the 4th Fluorine Chemistry Meeting, the 38th Autumn Semiannual Joint Meeting of the Chemical Society of Japan, Nagoya, October, 1978.

INTRODUCTION

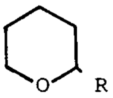
The electrochemical fluorination of aliphatic carboxylic acids has been known to afford besides perfluoroalkanoyl fluorides mixtures of perfluorocyclic ethers, which consist primarily of perfluoro(2-alkyloxolane)s (**3**), with isomeric perfluoro(2-alkyloxane)s (**2**) present in only small amounts [1].



Scheme 1

From α-alkyl-substituted valeric acids, we have shown that the perfluoro(2,4-dialkyloxolane)s and perfluoro(3-alkyloxane)s were obtained instead of **3** and **2** respectively [2]. However, no report has been appeared concerning the physical properties of these perfluoro(2-alkyloxane)s.

In a preliminary report, we have demonstrated electrochemical fluorinations of 2-methyloxane and 2-chloromethyloxane, which yielded the expected perfluoro(2-methyloxane) and perfluoro-(2-chloromethyloxane) in reasonable yields respectively [3]. The work has now been extended to the fluorination of such 2-alkyl-substituted oxanes(**1**)as 2-ethyl- (1a), 2-n-propyl- (1b), 2-iso-propyl- (1c), 2-n-butyl- (1d), and 2-n-amyl- (1e).



(**1**): R = C_2H_5 (1a), n-C_3H_7 (1b), iso-C_3H_7 (1c), n-C_4H_9 (1d), n-C_5H_{11} (1e)

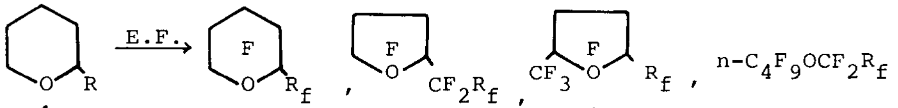
In order to make the authentic samples of perfluoro-(n-amyl n-butylether) (5d) and perfluoro(n-butyl n-hexylether) (5e) which were found to be formed as the cleaved products from respective fluorinations of 1d and 1e, fluorinations of n-amyl n-butylether (8) and n-butyl n-hexylether (9) were also conducted.

In the fluorination of **1**, the desired **2** was produced as a complex mixture composed mainly of isomeric perfluorooxolanes as well as perfluoro(dialkyl ether)s. An attempted successful purification of **2** which involves the reaction of a mixture of **2** and **3** with anhydrous aluminum chloride will also be reported in the present paper.

RESULTS AND DISCUSSION

The reaction conditions and the results of the fluorinations of 2-alkyl-substituted oxanes, and n-amyl n-butylether (8) and n-butyl n-hexylether (9) are shown in Table 1.

The fluorination of these cyclic and linear ethers proceeded quite smoothly and yielded the corresponding perfluoroethers in good yields. As shown in Scheme 2, it was found that the former yielded the desired perfluoro(2-alkyloxane)s (**2**) along with perfluoro(2-alkyloxolane)s (**3**), perfluoro(2-alkyl-5-methyloxolane)s (**4**) and perfluoro(dialkyl ether)s (**5**) in good yields, though in the case of 1c, the yield of the desired perfluoro(2-isopropyloxane) (2c) was small (Y=9.5%). Among these results, from 1d, fluorination products were obtained in a total yield of up to 45%. The low yield of 2c was due to the occurrence of the isomerization at a site of the iso-propyl group which changed into the n-propyl group during fluorination, as the yield of the perfluoro(2-n-propyloxane) (2b) formed was higher than that of 2c (Y=11.6%). While, the yields of the perfluorodialkyl ethers obtained from 8 and 9 were 10~15% at the best, that is, 14.4% for the perfluoro(n-amyl n-butylether) (5d) and 10.4% for the perfluoro(n-amyl n-hexylether) (5e) respectively.



1 **2** **3** **4** **5**

Y=23~28% 5~10% 2~12% 2~6%

a: $R=C_2H_5$, $R_f=C_2F_5$, b: $R=n\text{-}C_3H_7$, $R_f=n\text{-}C_3F_7$, c: $R=iso\text{-}C_3H_7$, $R_f=iso\text{-}C_3F_7$, d: $R=n\text{-}C_4H_9$, $R_f=n\text{-}C_4F_9$, e: $R=n\text{-}C_5H_{11}$, $R_f=n\text{-}C_5F_{11}$

Scheme 2

Compared with the dialkyl ethers, the cyclic ethers including oxanes and oxolanes have several advantages as the raw materials for the electrochemical fluorination. First, the solubility of the cyclic ethers in anhydrous hydrogen fluoride is larger than that of the dialkyl ethers due to the much stronger basic character of the former compounds. Second, the yields of the fluorinated ethers generally realized by the fluorination of

Table 1.

Results of the fluorinations of 2-alkyl-substituted oxanes and dialkyl ethers

Sample (mol)	Electricity passed (Ahr)	Fluorinated compounds obtained (g)	Perfluorocyclic ethers and perfluorodialkyl ethers obtained (Yield %)
1a (0.312)	217	52.9^a(4.2)^b	$n\text{-}C_4F_9OC_3F_7\text{-}n$ (5a)(3.9)^c, $\overline{CF(C_2F_5)CF_2CF_2CF(CF_3)O}$ (4a)(3.4), $\overline{CF(C_2F_5)(CF_2)_4O}$ (2a) + $\overline{CF(C_3F_7\text{-}n)(CF_2)_3O}$ (3a)(26.0), $\overline{CF_2CF(C_2F_5)(CF_2)_3O}$ (0.3).
1b (0.249)	230	31.8 (31.6)	$n\text{-}C_4F_9OC_4F_9\text{-}n$ (5b)(1.8), $\overline{CF(C_3F_7\text{-}n)CF_2CF_2CF(CF_3)O}$ (4b)(2.1), $\overline{CF(C_3F_7\text{-}n)(CF_2)_4O}$ (2b) + $\overline{CF(C_4F_9\text{-}n)(CF_2)_3O}$ (3b)(30.2), $\overline{CF_2CF(C_3F_7\text{-}n)(CF_2)_3O}$ (trace).
1c (0.252)	215	29.6 (22.8)	$\overline{CF(C_3F_7\text{-}iso)(CF_2)_4O}$ (2c) + $\overline{CF(C_3F_7\text{-}n)(CF_2)_4O}$ (2b) + $\overline{CF(C_4F_9\text{-}n)(CF_2)_3O}$ (3b)(23.5).
1d (0.235)	249	15.9 (53.8)	$n\text{-}C_4F_9OC_5F_{11}\text{-}n$ (5d)(3.8), $\overline{CF(C_4F_9\text{-}n)CF_2CF_2CF(CF_3)O}$ (4d)(11.6), $\overline{CF(C_4F_9\text{-}n)(CF_2)_4O}$ (2d) + $\overline{CF(C_5F_{11}\text{-}n)(CF_2)_3O}$ (3d)(29.7).

1e (0.203)	218	12.6 (49.8)	n-$C_4F_9OC_6F_{13}$-n (5e) (3.6), $\overline{CF(C_5F_{11}\text{-n})CF_2CF_2CF(CF_3)O}$ (4e) (11.5), $\overline{CF(C_5F_{11}\text{-n})(CF_2)_4O}$ (2e) + $\overline{CF(C_6F_{13}\text{-n})(CF_2)_3O}$ (3e) (23.1).
8 (0.163)	185	30.4 (14.2)	5d (14.4)
9 (0.087)	125	8.3 (7.2)	5e (10.4)

a) Products obtained in cold traps. b) Products obtained as cell drainings. c) Arranged in order of the ellution time in the GLC spectrum (Col. C). See the experimental section.

cyclic ethers is considerably high as compared with those obtained from the fluorination of dialkyl ethers. The reason for this may be interpreted as being due to having a possibility of forming either an oxane- or an oxolane ring again via radical process, even if the carbon oxygen bond of the original cyclic ethers may be cleaved in the initial stage of the fluorination. Such an intramolecular cyclization is a well-known side reaction in the electrochemical fluorination of aliphatic carboxylic acids [1].

Among these by-products, **4** and **5** could be easily separated by GLC from the desired **2** . However, **2** and **3** formed an inseparable mixture and an attempt to purify them by means of GLC was unsuccessful. Presumably, the difficulties of the separation of these two compounds may be the main reason why **3** has not been characterized yet. Hence, its constituent ratio was determined by studying the ^{19}F nmr data of the mixture of **2** and **3** ; with respective to the geminal fluorines of the α carbon to oxygen, the absorption peaks due to the α CF_2- group of **2** appears at $\phi 78.2 \sim 78.6$ ppm and $\phi 91.8 \sim 92.3$ ppm with $J_{AB} = 156 \sim 160$ Hz, while those of **3** at $\phi 82.3 \sim 82.9$ ppm and $\phi 84.6 \sim 84.9$ ppm with $J_{AB} = 132 \sim 138$ Hz respectively, which are very easy to distinguish from each other [3]. The mixing ratios of **2** to **3** were found to be in the range of 1 : $0.11 \sim 0.37$.

The structural determination of these purified products was carried out on the basis of their spectroscopic data (mass, infrared and ^{19}F nmr) and elemental analyses (C and F). In Table 2 are shown the physical properties of **4** and **5** , and in Table 6 the ^{19}F nmr data of **5** respectively.

Except **4** , these products were straightforwardly assigned to their proposed structures. In the case of **4** , its ^{19}F nmr spectra were very complicated partly because it consisted of a mixture of cis- and trans isomers. However, it showed clearly the presence of CF_3- groups at $\phi 80.6 \sim 81.5$ ppm and CF_2- groups, being not adjacent to oxygen, at $\phi 118.5 \sim 137.5$ ppm respectively. Its mass spectra gave no molecular ions but showed the significant fragments corresponding $[M-CF_3]^+$ and $[M-R_f]^+$ where CF_3- and R_f- represented the perfluoroalkyl groups at the 2 and 5 positions of the oxolane ring respectively. The largest ions observed were

Table 2.

Properties of 2a, 2b, 2d, 2e, 4a, 4b, 4d, 4e, 5a, 5b, 5d and 5e

Compound[a]	BP(°C)[b]	d_4^{20}	n_D^{20}	Elemental Analysis	
				C(%)	F(%)
2a	73.7 ~ 73.5	1.7604	<1.28	23.03	71.5
				(22.95)[c]	(72.7)
2b	94.5 ~ 95.5	1.7940	1.2816	22.87	73.6
				(23.08)	(73.1)
2d	116.0~116.8	1.8264	1.2883	23.07	73.0
				(23.18)	(73.4)
2e	137.0~138.0	1.8496	1.2912	23.19	72.8
				(23.26)	(73.6)
4a	68.0 ~ 68.3	1.7160	<1.28	22.65	71.7
				(22.95)	(72.7)
4b	92.0 ~ 92.5	1.7517	<1.28	23.23	72.6
				(23.08)	(73.1)
4d	114.0~114.7	1.7815	<1.28	22.97	74.3
				(23.18)	(73.4)
4e	133.2~133.7	1.8046	1.2822	23.00	73.5
				(23.26)	(73.6)
5a	68.5 ~ 69.5	1.6861	<1.28	20.65	76.8
				(20.79)	(75.3)
5b	97.0 ~ 97.3	1.7274	<1.28		
5d	110.5~111.5	1.7580	<1.28	21.31	74.8
				(21.43)	(75.4)
5e	126.0~127.3	1.7939	<1.28	21.52	75.3
				(21.66)	(75.5)

a) Except 5b, all of these are new compounds. b) Boiling points are not corrected. c) Calculated values in parentheses.

[M-F]$^+$ ions as usual. Thus, on the basis of these observations as well as elemental analysis, we assigned them as the proposed perfluoro(2-alkyl-5-methyloxolane)s.

The purification of **2** containing small amounts of **3** was finally achieved by means of the chemical method which consisted of allowing these mixtures to treat with anhydrous AlCl$_3$.

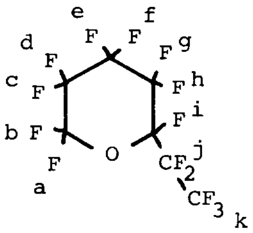
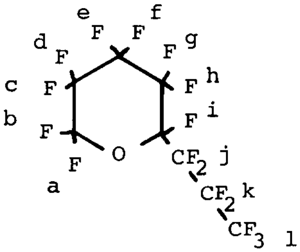
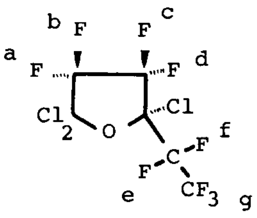
Previously, we have reported some reactions of the perfluoro-(2-alkyloxolane)s and perfluoro(2-methyloxane) with anhydrous AlCl$_3$ respectively [3,4]. From these experiments, the following few points were observed. 1. Perfluoro(2-methyloxolane) began to react around 143 °C yielding the corresponding perfluoro(2,5,5-trichloro-2-methyloxolane)s. And as the perfluoroalkyl groups of the perfluoro(2-alkyloxolane)s became larger, an increasingly higher reaction temperature was needed [for example, for perfluoro(2-n-butyloxolane), the minimum reaction temperature as high as 170 °C was needed to give the perfluoro(2,5,5-trichloro-n-butyloxolane)]. 2. Perfluoro(2-methyloxane) did not react at around 160 °C at all. By raising the reaction temperature to near 190 °C, it reacted affording only such perchlorinated compounds as $COCl_2$, CCl_4, C_2Cl_6, C_6Cl_6 and a tarry material. These results seemed to suggest that the perfluoro(2-alkyloxolane)s would react with anhydrous $AlCl_3$ more easily than the perfluoro(2-alkyloxane)s. However, following experiments revealed that there was not any distinct difference between **2** and **3** in the reactivity toward anhydrous $AlCl_3$. Thus, the mixture of **2** and **3** was treated with excess amounts of anhydrous $AlCl_3$ at such a reaction temperature as the former would not react but only the latter would change into the corresponding α,α,α'-trichlorinated perfluorooxolanes.

Initially, to determine the optimum reaction temperature, several reactions of a mixture of 2a and 3a with excess amounts of anhydrous $AlCl_3$ were investigated at various temperatures in a range of 150$\sim$ 190 °C [Table 3]. It was observed that the chlorination both of 2a and 3a initiated around 150 °C yielding not only the expected perfluoro(2,5,5-trichloro-2-n-propyloxolane) (6a) but also perfluoro(5,5-dichloro-n-heptanoyl chloride) (7a) as the products. In addition, as the reaction temperature was raised, the amounts both of 2a recovered and the chlorinated products (6a and 7a) were found to be decreased concomitantly because of the extensive advance of the chlorination of 6a and 7a. Therefore, in order to recover the unreacted **2** freed from **3** , the application of the minimum reaction temperature ($\sim$150 °C) and the prolonged reaction time ($\sim$48 hrs) was required.

Utilizing these results, respective reactions of the mixtures of **2** and **3** were carried out. For purposes of comparison, the reaction of a mixture of perfluoro(2-methyloxane) (2f) and perfluoro(2-ethyloxolane) (3f) with anhydrous $AlCl_3$ was also conducted similarly. Thus, in each experiments, pure **2** was obtained successfully. These results are summarized in Table 4. In Table 2 and Fig. 1, the physical properties of pure **2** together with those of other fluorination products and the ^{19}F nmr data of **2** with those of **6** are shown respectively.

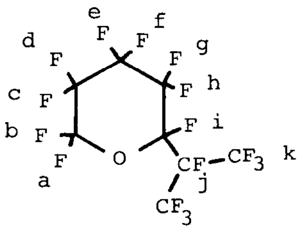
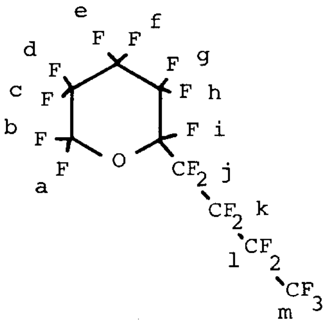
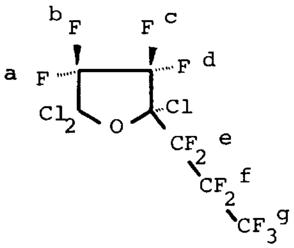
Fig. 1.

^{19}F nmr data of 2a, 2b, 2c, 2d, 2e, 6a, 6d, 6e and 6f

Compd	Formula		Chemical shift^{a,b} (ppm)		J (Hz)
2a		a	78.5	J_{AB}	a-b=156,
		b	92.3		c-d=300,
		c	122.1	J_{AB}	e-f=284,
		d	131.4		g-h=278,
		e	125.5	J_{AB}	k-i=12.5,
		f	141.6		k-g=2.8,
		g	123.9	J_{AB}	k-h=2.8
		h	139.3		
		i	125.8		
		j	131.2		
		k	81.0		
2b		a	92.2	J_{AB}	a-b=158,
		b	78.6		e-f=284,
		c			g-h=278,
		d			l-j=9.9,
		e		J_{AB}	l-i=2.7
		f			
		g		J_{AB}	
		h			
		i			
		j			
		k	125.6		
		l	81.6		
6f		a	113.1	J_{AB}	a-b=228,
		b	120.3		a-d=14.1,
		c	123.5	J_{AB}	c-d=237,
		d	108.3		g-b=1.9,
		e			g-c=5.0
		f			
		g	78.3		

(continued on following page)

Fig. 1. (continued)

<u>2c</u>		a	78.2	J_{AB}	a-b=158,
		b	91.8		e-f=284,
		c			g-h=280,
		d			k-i=82
		e		J_{AB}	
		f			
		g		J_{AB}	
		h			
		i			
		j	185.2		
		k	71.9		
<u>2d</u>		a	78.6	J_{AB}	a-b=158,
		b	92.2		c-d=298,
		c		J_{AB}	e-f=284,
		d			g-h=276,
		e		J_{AB}	m-k=10.3,
		f			m-j=2.5
		g		J_{AB}	
		h			
		i			
		j			
		k	121.9		
		l	126.3		
		m	81.6		
<u>6a</u>		a	111.3	J_{AB}	a-b=228,
		b	119.5		a-d=13.6,
		c	121.9	J_{AB}	c-d=244,
		d	107.6		g-e=10.6
		e	115.1		
		f	120.6		
		g	80.6		

a) ϕ value (ppm relative to internal CCl_3F). b) Only obvious chemical shifts and coupling constants are given.

(continued on facing page)

Fig. 1. (continued)

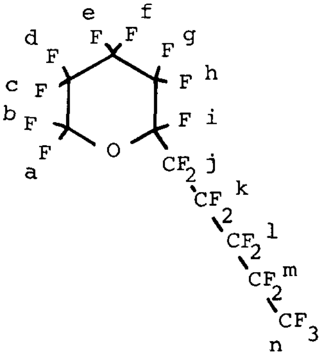
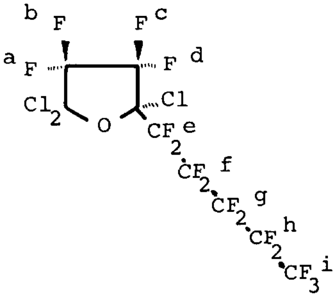
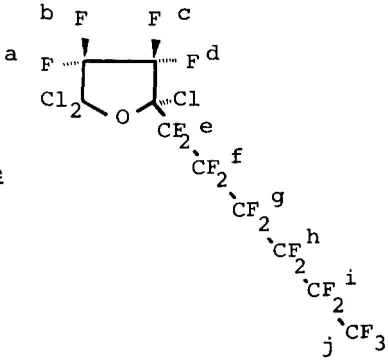
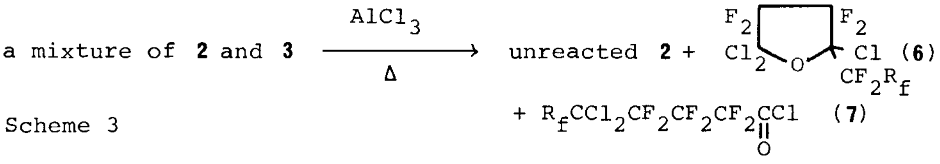
<u>2e</u>		a	78.4	J_{AB}	a-b=160,
		b	92.1		e-f=286,
		c			g-h=278,
		d			n-l=10.4,
		e		J_{AB}	n-k=2.5
		f			
		g		J_{AB}	
		h			
		i			
		j			
		k	120.8		
		l	122.6		
		m	126.2		
		n	81.5		
<u>6d</u>		a	112.1	J_{AB}	a-b=226,
		b	120.7		a-d=13.6,
		c	122.8	J_{AB}	c-d=240,
		d	109.8		i-g=10.2,
		e	115.0		i-f=2.6
		f	117.5		
		g	123.1		
		h	126.4		
		i	81.6		
<u>6e</u>		a	112.6	J_{AB}	a-b=230,
		b	116.2		c-d=240,
		c	122.5	J_{AB}	a-d=14.1,
		d	109.1		j-h=10.1,
		e	114.9		j-g=2.5
		f	117.6		
		g	122.0		
		h	122.7		
		i	126.6		
		j	81.6		

Table 3.

Summary of reactions of a mixture of 2a and 3a with anhydrous $AlCl_3$ at various temperatures

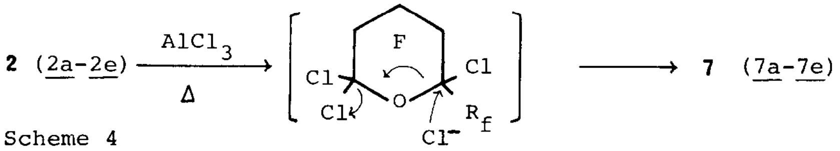
Sample (mmol) [a]	Reaction conditions		Sample recovered (mmol)	Purity of 2a	Product (%) [b]	
	temp (°C)	time (hr)			6a	7a
4.93	150	20	3.75	95.6	14.7	trace
4.87	150	45.5	2.68	100	19.9	17.1
4.76	160	20	2.19	100	23.0	27.0
4.86	170	20	1.77	100	7.6	8.5
4.97	190	20	1.59	100	2.9	3.3

a) A mixture of 2a (87.0%) and 3a (13.0%) was treated with an 2 molar excess of $AlCl_3$. b) The yields of products were caluculated based on the sample consumed.



Scheme 3

It should be noted that, being different from the reaction of **3** (3a-3f), the reaction of **2** (2a-2e) with anhydrous $AlCl_3$ yielded the perfluoro(5,5-dichloroalkanoyl chloride)s (**7**) as the sole chlorination product in place of the corresponding α,α,α'-trichloro-substituted perfluorooxanes. The formation of **7**



Scheme 4

might be considered via the supposed α,α,α'-trichlorinated compound as a result of the scission of the bond between oxygen and C_2. However, it is not clear why the expected perfluoro(5,5-dichlorohexanoyl chloride) was not formed from the reaction of 2f with $AlCl_3$ unlike other perfluoro(2-alkyloxane)s (2a-2e).

The physical properties of **6** and **7** obtained are summarized in Table 5, and the ^{19}F nmr data of **7** are presented in Table 6 together with those of **5** , respectively.

Table 4.
Summary of reactions of a mixture of **2** (a,b,d-f) and **3** (a,b,d-f) with anhydrous $AlCl_3$[a]

Sample [**2**/ **3** ratio] (mmol)	Reaction conditions temp (°C) time (hr)	Pure **2** recovered (mmol)	Product[b] (%)
2a + 3a [1 : 0.149] (14.51)	155/24	5.9	6a (26.9) 7a (41.9)
2b + 3b [1 : 0.364] (4.23)	155/46	2.3	6b (33.6) 7b (14.2)
2d + 3d [1 : 0.276] (9.58)	160/43	3.9	6d (34.4) 7d (45.4)
2e + 3e [1 : 0.152] (5.58)	160/47	2.6	6e (18.2) 7e (38.0)
2f + 3f [1 : 0.326] (5.36)	155/30	2.54	6f (38.7)

a) A 2 molar excess of $AlCl_3$ was used. b) The yields of products were calculated based on the sample consumed.

Table 5.
Properties of 6a, 6b, 6d, 6e, 6f, 7a, 7b, 7d and 7e

Compound[a]	Bp(°C)[b]	d_4^{20}	n_D^{20}	Elemental Analysis C(%)	 F(%)
6a	146.0~147.0	1.8012	1.3545	20.24 (20.22)	50.5 (50.3)
6b	164.0~164.5	1.8275	1.3523		
6d	183.5~184.9	1.8421	1.3510	20.72 (20.95)	57.1 (55.3)
6e	195~200		1.3476	21.20 (21.22)	56.1 (57.1)
6f	131.0~131.5	1.7815	1.3597		
7a	139.5~140.0	1.7649	1.3497	20.21 (20.22)	51.0 (50.3)
7b	167.5~168.0	1.7905	1.3473	20.74 (20.62)	52.5 (53.1)
7d	178.5~180.5	1.8068	1.3447	21.19 (20.95)	53.7 (55.3)
7e	197~199	1.8321	1.3433	21.34 (21.22)	56.4 (57.1)

a) Except 6b and 6f, all of these are new compounds. b) Boiling points are not corrected. c) Calculated values in parentheses.

Table 6.

^{19}F nmr data of 5a, 5b, 5d, 5e, 7a, 7b, 7d and 7e

Compd	Formula	Chemical shift (ppm)[a] A	B	C	D	E	F	G	H	I	J
5a	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}O\underset{E}{CF_2}\underset{F}{CF_2}\underset{G}{CF_3}$	82.4 t^{b}	130.1 m	126.4 m	82.2 m	84.1 m	126.4 m	82.2 t^{c}			
5b	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}OCF_2CF_2CF_2CF_3$	82.1 t^{d}	127.0 m	127.0 m	83.7 m						
5d	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}O\underset{E}{CF_2}\underset{F}{CF_2}\underset{G}{CF_2}\underset{H}{CF_2}\underset{I}{CF_3}$	81.6 $t\text{-}t^{e}$	125.8 m	123.1 m	83.4 m	83.4 m	123.1 m	126.4 m	126.6 m	81.8 t^{f}	
5e	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}O\underset{E}{CF_2}\underset{F}{CF_2}\underset{G}{CF_2}\underset{H}{CF_2}\underset{I}{CF_2}\underset{J}{CF_3}$	82.0 $t\text{-}t^{g}$	126.0 m	123.1 m	83.3 m	83.3 m	123.1 m	123.1 m	126.7 m	127.2 m	82.3 t^{h}
7a	$\underset{A}{CF_3}\underset{B}{CF_2}CCl_2\underset{C}{CF_2}\underset{D}{CF_2}\underset{E}{CF_2}C(O)Cl$	81.3 t^{i}	120.1 $t\text{-}t^{j}$	116.9 $t\text{-}t^{k}$	114.3 m	107.1 m					
7b	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}CCl_2\underset{D}{CF_2}\underset{E}{CF_2}\underset{F}{CF_2}C(O)Cl$	81.3 t^{l}	126.3 m	118.2 m	118.2 m	115.3 m	108.2 m				
7d	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}CCl_2\underset{E}{CF_2}\underset{F}{CF_2}\underset{G}{CF_2}C(O)Cl$	81.8 $t\text{-}t^{m}$	126.2 m	122.7 m	117.9 m	117.9 m	115.4 m	108.3 m			
7e	$\underset{A}{CF_3}\underset{B}{CF_2}\underset{C}{CF_2}\underset{D}{CF_2}\underset{E}{CF_2}CCl_2\underset{F}{CF_2}\underset{G}{CF_2}\underset{H}{CF_2}C(O)Cl$	80.9 $t\text{-}t^{n}$	125.9 m	121.8 m	121.0 m	116.9 m	116.9 m	114.5 m	107.5 m		

a) ϕ value, to center of peak or multiplet: t = triplet, m = multiplet. b) J(A-C) = 7.1 Hz. c) J(G-E) = 9.6. d) J(A-C) = 9.4. e) J(A-C) = 10.0, J(A-D) = 2.3. f) J(I-G) = 9.2. g) J(A-C) = 10.3, J(A-D) = 2.9. h) J(J-H) = 9.4. i) J(A-C) = 3.1. j) J(B-C) = J(C-B) = 13.2, J(B-D) = 6.2. k) J(C-E) = 13.1. l) J(A-C) = 8.8. m) J(A-C) = 10.1, J(A-D) = 1.9. n) J(A-C) = 9.9, J(A-D) = 2.6.

EXPERIMENTAL

Reagents

The 2-alkyl-substituted oxanes used were prepared by the reaction of 2-chlorooxane with appropriate grignard reagents according to the method described in the literature [5]. The n-amyl n-butylether and n-butyl n-hexylether were prepared by the usual Williamson reaction from n-amyl bromide (Tokyo Kasei Co.) and n-butyl alcohol (Tokyo Kasei Co.), and from n-butyl bromide (Tokyo Kasei Co.) and n-hexyl alcohol (Tokyo Kasei Co.) respectively. These starting materials which should be fluorinated had the following boiling points; 2-ethyloxane, bp 127.0～128.5 °C (lit. bp 127～8 °C) [5], 2-n-propyloxane, bp 148.0～151.5 °C (lit. 152～3 °C) [5], 2-iso-propyloxane, bp 138.0～145.5 °C (lit. 144～5 °C) [5], 2-n-butyloxane, bp 174.0～178.0 °C (lit. 176～7 °C) [5], 2-n-amyloxane, bp 105.0～110.5 °C/45 mm Hg, n-amyl n-butylether, bp 78.5～80.5 °C/64 mm Hg (lit. 83.7～84.7 °C/50 mm Hg) [6], n-butyl n-hexylether, bp 89.0～90.0 °C/45 mm Hg.

A mixture of perfluoro(2-methyloxane) and perfluoro(2-ethyloxolane) used for the reaction with anhydrous $AlCl_3$ (Kishida Chemicals Co.) was prepared by the electrochemical fluorination of 2-methyloxane (Aldrich Chemical Co.) [3].

Anhydrous hydrogen fluoride (Daikin Industries Co.) was more than 99.9% pure.

Apparatus

Fluorination was carried out in the usual way [2] using a 1*l* electrolytic cell fitted with a reflux condenser (-20 °C) on the top of the cell: the electrodes were consisted of 8 anodes and 9 cathodes arranged alternatively. The effective anodic surface area was 9.2 dm^2.

Hoke bombs (capacity: 30 m*l*) with stainless steel valves were used for the reaction of a mixture of **2** and **3** with anhydrous $AlCl_3$, and a pyrex vacuum line equipped with a Heise Bourdon Tube gauge was used for handling the volatile compounds.

Analytical work was carried out with a Shimadzu GC-2C gas chromatograph using stainless columns (3 mm dia) packed with

20% diester of hexamethylene glycol with perfluorooctanoic acid on Chromosorb PAW (6.4 m)(Col. A), 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane on Chromosorb PAW (6.4 m)(Col. B), 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (6.4 m)(Col. C), and 26% Kel F #90 on Chromosorb PAW (3.8 m) (Col. D). For a semi-preparative work, a Shimadzu GC-1C gas chromatograph was used employing stainless columns (10 mm dia) packed with 30% Silicone QF-1 on Chromosorb PAW (4.9 m)(Col. E), 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane on Chromosorb PAW (4.9 m)(Col. F), 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (4.9 m)(Col. G), and 30% Kel F Wax on Chromosorb PAW (4.9 m)(Col. H). The carrier was helium in all cases.

Infrared spectra were measured on a Hitachi EPI-G3 spectrometer, using a 6 cm gas cell with KBr windows unless otherwise stated. ^{19}F nmr spectra were measured on a Hitachi R-20B high resolution spectrometer operating at 56.46 MHz using CCl_3F as an internal standard. Mass spectra were measured on a Hitachi RMU-7 instrument at 70 eV.

§ Fluorination of 2-alkyl-substituted oxanes

Fluorination of 1a

Sample 1a (35.6 g, 0.312 mol) was charged into the cell which contained 1l electrochemically purified anhydrous hydrogen fluoride, and the solution was subjected to fluorination with an anodic current density of 3.5 A/dm^2, a cell voltage of 5.2∼9.0 V and a cell temperature of 5∼6 °C over a period of 409 min (217 Ahr). The volatile products (52.9 g) were collected in traps at -196 °c after passing through the consecutive gas washing bottles containing aqueous potassium hydroxide and potassium sulfite solution, and the products sunk at the bottom of the cell (4.2 g), i.e. cell drainings, were drained from it after the complition of the electrolysis.

Preceding to the distillation of the products collected at cold traps, the compounds having lower bps than room temp were roughly separated from other products by use of the traps of a low-temperature distillation unit. These very volatile compounds

(2.0 g) consisted primarily of CF_4 (10), and small amounts of CHF_3 (11), C_2F_6 (12) and C_3F_8 (13) (analysed by GLC using Col.A). The remaining products (50.9 g) were fractionally distilled into 3 portions, and these fractions and cell drainings were subsequently analysed by GLC (Col. B). Each products except new one, were identified by comparison of their infrared spectra and retention times on a gas chromatogram with those of the authentic samples. In the case of the new compounds, they were separated from other products by use of semi-preparative GLC, and their structure was determined on the basis of their ^{19}F nmr and mass spectra, and elemental analysis. Fraction 1, bp room temp∼48.3 °C, 4.7 g; [product (compound number), g yield], n-C_4F_{10} (14) (0.5) perfluorooxolane (15) (0.3), n-C_5F_{12} (16) (0.1), iso-C_5F_{12} (17) (0.3), perfluoro(2-methyloxolane) (18) (0.4), perfluoro(3-methyloxolane) (19) (0.3), perfluorooxane (20) (1.6), n-C_6F_{14} (21) (0.2), 5a (trace), 4a (trace), 2a + 3a (0.4), unidentified (0.3). Fraction 2, bp 48.4 ∼46.8 °C, 9.2 g, 20 (0.4), 21 (1.1), 5a (1.0), 4a (1.0), 2a + 3a (4.6), unidentified (1.1). Fraction 3, bp 64.9∼81.0 °C, 28.0 g, 5a (3.2), 6a (2.3), 2a + 3a (19.6), unidentified (2.8), Residue, 3.4 g, 5a (0.2), 4a (0.2), 2a + 3a (2.3), perfluoro(3-ethyloxolane) (22) (0.2), unidentified (0.5). Cell drainings, 4.2 g, 5a (0.4), 4a (0.3), 2a + 3a (2.9), 22 (0.2), unidentified (0.5). Among these products, 5a, 4a and a mixture of 2a and 3a were isolated from other products by GLC (Col. E, F, G), and were characterized spectroscopically. Based on the relative areas of the absorption peaks due to the α CF_2- groups in the ^{19}F nmr spectrum of a mixture of 2a and 3a, the constituent ratio was determined to be 2a/3a = 1 : 0.149. Perfluoro(n-butyl n-propylether) (5a) (nc): IR: 1345 (w), 1303 (m), 1252 (vs), 1228 (s,sh), 1163 (s), 1134 (m), 1104 (w), 1003 (m), 899 (m), 753 (w), 735∼710 (w) cm^{-1}. Mass: 235 $[M-F]^+$, 219 $[C_4F_{10}^+]$, 169 $[C_3F_7^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 100 $[C_2F_4^+]$, 69 $[CF_3^+]$. Perfluoro(2-ethyl-5-methyloxolane) (4a) (nc): IR: 1368 (w,sh), 1348 (w), 1334 (ms), 1296 (w), 1266 (s), 1248 (vs), 1231 (s), 1204 (m), 1161 (m), 1135 (ms), 1107 (s), 1039 (w), 1019 (w), 923 (m), 856 (w), 829 (m), 749 (m), 725 (m), 602 (m) cm^{-1}. Mass: 347 $[M-F]^+$, 297 $[M-CF_3]^+$, 247 $[M-C_2F_5]^+$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 100 $[C_2F_4^+]$, 97 $[C_3F_3O^+]$, 69 $[CF_3^+]$. Perfluoro(3-ethyloxane) (22) [2]: IR: 1365 (w,sh), 1350 (m), 1311 (ms,sh), 1298 (s), 1269 (s,sh), 1237∼1250 (vs), 1224 (s,sh), 1190 (m,sh), 1179 (ms), 1147 (s), 1097 (m), 1078 (s), 1014 (m), 1000 (m), 943 (w), 858 (m), 840 (w), 829 (m), 791 (w), 747 (m), 712 (m), 676 (w), 642 (w), 611 (w), 497 (w) cm^{-1}. Mass: 347 [$C_7F_{13}O^+$], 231 [$C_5F_9^+$], 181 [$C_4F_7^+$], 131 [$C_3F_5^+$], 119 [$C_2F_5^+$], 100 [$C_2F_4^+$], 93 [$C_3F_3^+$], 69 [CF_3^+]. Physical properties and analytical data of 5a and 4a, and ^{19}F nmr data of 5a are shown in Tables 2 and 6 respectively.

Fluorination of 1b

Sample 1b (31.9 g, 0.249 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.1∼9.0 V, 5∼6 °C, 432 min (230 Ahr). The products weighed 31.8 g for those collected at -196 °C trap and 31.6 g for cell drainings respectively. Work-up of the products was the same as those explained for the fluorination of 1a. Thus, the following compounds were obtained; Fraction 1, bp room temp∼47.0 °C, 3.7 g; (compound number, g yield), 14 (1.0), 15 (0.3), 16 (0.1), 17 (0.3), 18 (0.3), 19 (0.2), 20 (0.9), 21 (0.1) unidentified (0.3). Fraction 2, bp 47.1∼49.3 °C, 2.4 g, 20 (0.1), 21 (0.2), n-C_7F_{16} (23)(1.0), 5b (0.2), 4b (0.2), 2b + 3b (0.3), unidentified (0.6). Fraction 3, bp 49.4∼105.3 °C, 10.8 g, 23 (0.4), 5b (1.2), 4b (1.8), 2b + 3b (6.3), unidentified (1.0). Residue, 5.5 g, 5b (0.5), 4b (0.2), 2b + 3b (3.8), perfluoro-(3-n-propyloxane) (24)(0.2), unidentified (0.7). Cell drainings, 31.6 g, 23 (0.7), 5b (2.7), 4b (2.8), 2b + 3b (20.8), 24 (0.9), unidentified (3.7). Perfluoro(2-methyl-5-n-propyloxolane) (3b) (nc): IR: 1349 (ms), 1303 (m), 1281 (m,sh), 1250∼1258 (vs), 1231 (s,sh), 1211 (s), 1160 (m), 1146 (ms), 1107 (s), 1096 (ms,sh), 1077 (m,sh), 980 (w), 962 (w), 915 (w), 900 (m), 845 (w), 813 (w), 795 (w), 749 (w,sh), 738 (w), 722 (m), 584 (w) cm^{-1}. Mass: 398 $[M-F]^+$, 347 $[M-CF_3]^+$, 247 $[M-C_3F_7]^+$, 131 [$C_3F_5^+$], 119 [$C_2F_5^+$], 100 [$C_2F_4^+$], 97 [$C_2F_3O^+$], 69 [CF_3^+]. Perfluoro(3-n-propyloxane) (24)[2]: IR: 1349 (ms), 1315 (s), 1291 (s), 1272 (vs), 1248 (vs), 1224 (vs), 1205 (ms,sh), 1176∼1186 (ms), 1150 (s), 1130 (s), 1029 (ms), 1001 (ms), 905 (w), 835 (m), 806 (m), 786 (w), 739 (ms), 713 (m), 672 (m), 643 (w), 628 (w), 609 (w), 568 (w), 536 (w), 498 (m) cm^{-1}. Mass: 397 $[M-F]^+$, 231 [$C_5F_9^+$], 181 [$C_4F_7^+$], 169 [$C_3F_7^+$], 131 [$C_3F_5^+$], 119 [$C_2F_5^+$], 100 [$C_2F_4^+$], 69 [CF_3^+].

Based on the relative areas of the absorption peaks due to the α CF_2- groups in the ^{19}F nmr spectrum of a mixture of 2b and 3b, the constituent ratios of the mixture of 2b and 3b were found to be 2b/3b = 1 : 0.239 for the compounds isolated from Fraction 3 and Residue, and 1 : 0.364 for those isolated from cell drainings respectively. Physical properties and analytical data of 4b is given in Table 2.

Fluorination of 1c

Sample 1c (32.2 g, 0.252 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.1∼9.0 V, 5∼6 °C, 402 min (215 Ahr).

The amounts of the products were 29.6 g for those collected at -196 °C trap and 22.8 g for those of cell drainings respectively. Work-up of the products was almost the same as those explained for the fluorination of 1a and 1b. In this experiments, however, many kinds of products were produced due to the isomerization of the iso-propyl group to the n-propyl group as well as the ring isomerization during fluorination, which made the isolation of each products still more difficult. Therefore, only the one fraction corresponding to the largest peak in the gas chromatogram was isolated by GLC (Col. E, G). Its amount was 8.3 g for the fraction separated from the product at cold traps, and 16.5 g for that separated from the cell drainings respectively. These fractions were found to be composed of three kinds of perfluorocyclic ethers including the expected 2c by ^{19}F nmr spectroscopy.

On the basis of the relative areas of the absorption peaks due to the α CF_2- groups in the ^{19}F nmr spectrum of the combined sample of these fractions, the following composition was determined; 2c + 2b (89.5%) and 3b (10.5%). The constituent ratio of the mixture of 2c and 2b was further determined by the integration of the absorption peaks due to each of the CF_3- groups (φ71.9 ppm for the CF_3- group of 2c and φ81.5 ppm for the CF_3- group of 2b, respectively) in the ^{19}F nmr spectrum of a mixture of these compounds. Thus, the composition of these cyclic ethers was found to consist of 2c (40.5%), 2b (49.0%) and 3b (10.5%) respectively.

Fluorination of 1d

Similarly, 1d (33.4 g, 0.235 mol) was fluorinated under the following conditions; 3.5 A/dm^2, 5.5∼9.0 V, 5∼6 °C, 457 min (249 Ahr).

The products weighed 15.9 g for those collected at cold traps and 53.8 g for cell drainings respectively. Work-up of the products was the same as those described in the fluorination of 1b. Thus, the following compounds were obtained; Fraction 1, bp room temp∼41.0 °C, 4.0 g, 13 (0.1 g), 14 (1.2), 15 (0.2), 16 (1.0), 17 (0.3), 18 (0.3), 19 (0.2), 20 (0.6), unidentified (0.2). Fraction 2, bp 41.4∼52.8 °C, 0.9 g, 16 (0.3), 17 (0.1), 18 (0.1), 20 (0.2), unidentified (0.2). Residue, 5.8 g, 21 (0.1), 23 (0.9), 25 (0.6), 5d (0.5), 4d (1.1), 2d + 3d (1.7), unidentified (0.9). Cell drainings, 53.8 g, 25 (1.8), 5d (4.0), 4d (11.7), 2d + 3d (30.8), unidentified (0.9). Based on the relative areas of the absorption peaks due to the α CF_2- groups in the ^{19}F nmr spectrum of a mixture of 2d and 3d, the constituent ratio was determined to be 2d/3d = 1 : 0.276. Perfluoro(2-n-butyl-5-methyloxolane) (4d)(nc): IR: 1346 (m), 1303 (w), 1252 (vs), 1233 (s,sh), 1218 (ms,sh), 1198 (m), 1157 (ms), 1121 (m), 1103 (ms), 1028∼1058 (w), 943∼958 (w), 897 (w), 881 (w), 837 (w), 817 (w), 806 (w), 777 (w), 713 (w), 638 (w), 593 (w), 533 (w), 480 (w) cm^{-1}. Mass: 447 $[M-F]^+$, 397 $[M-CF_3]^+$, 247 $[M-C_4F_9]^+$, 169 $[C_3F_7^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 100 $[C_2F_4^+]$, 69 $[CF_3^+]$. IR spectrum of 5d was identical with that of the authentic one prepared by the fluorination of 8. Physical properties and analytical data of 4d are shown in Table 2.

Fluorination of 1e

Similarly, 1e (32.1 g, 0.203 mol) was fluorinated under the following conditions; 3.5 A/dm^2, 5.8∼8.7 V, 5∼6 °C, 404 min (218 Ahr). The products weighed 12.6 g for those collected at cold traps and 49.8 g for cell drainings respectively. As the products collected at cold traps consisted mostly of compounds having bps higher than room temp, they were analysed directly by means of GLC without being fractionally separated. Thus, the following compounds were obtained; 13 (1.0 g), 14 (1.9), 15 (0.7), 16 + 18 (2.7), 20 (1.1), 21 (1.7), unidentified (3.7). Cell drainings, 49.8 g, 5e (4.0), 4e (12.1), 2e + 3e (24.2), unidentified (9.5). Based on the relative areas of the absorption peaks due to the α CF_2- groups in the ^{19}F nmr spectrum of a mixture of 2e and 3e, the constituent ratio was found to be 2e/3e = 1 : 0.276. Perfluoro(2-n-amyl-5-methyloxolane) (4e)(nc): IR (film): 1294 1344 (m,broad), 1174∼1244 (s∼vs, broad), 1150 (s), 1131 (s), 1119 (ms,sh), 1048 (ms), 1014 (w), 921 (w), 864 (w), 856 (w), 835 (w), 813 (w), 773 (w), 746 (m), 741 (m), 729 (m), 714 (ms), 686 (w), 643∼654 (w), 564∼596 (w), 533 (w) cm^{-1}. Mass: 497 $[M-F]^+$, 297 $[M-C_4F_9]^+$, 247 $[M-C_5F_{11}]$, 181 $[C_4F_7^+]$, 169 $[C_3F_7^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 69 $[CF_3^+]$. The IR spectrum of 5e was identical with that of the authentic one prepared by the flurination of 9. Physical properties and analytical data of 4e are shown in Table 2.

Fluorination of 8

Similarly, 8 (23.4 g, 0.163 mol) was fluorinated under the following conditions; 3.5 A/dm^2, 4.1∼8.0 V, 5∼6 °C, 345 min (185 Ahr). The products weighed 30.4 g for those collected at cold traps and 14.2 g for cell drainings respectively. The products at cold traps were fractionated by low-temperature distillation into four portions, and each of them was analysed by GLC (Col. A,B,C) similarly. Thus, the following compounds were obtained; Fraction 1, 0.3 g, -99.0∼-44.8 °C, 10 (0.3 g), 11 (trace), 12 (trace). Fraction 2, 2.7 g, -40.5∼-4.7 °C, 10 + 11 + 12 (0.9), 13 (1.5), unidentified (0.3). Fraction 3, 10.1 g, -4.8∼-1.1 °C, 13 (0.4), 14 (8.8), unidentified (1.0). Fraction 4, ∼room temp, 12.9 g, 14 (0.7), 15 (0.2), 16 (4.3), 17 (1.0), 18 (3.4), 20 (1.3) unidentified (2.0). Hold up, 4.4 g, 5d (1.8), unidentified (2.5). Cell drainings, 14.2 g, 5d (10.0), unidentified (4.2). Perfluoro-(n-amyl n-butylether) (5d)(nc): IR: 1350 (w,sh), 1335 (m), 1307 (ms), 1252 (vs), 1227 (vs), 1198 (ms,sh), 1158 (s), 1138 (ms,sh), 1125 (m,sh), 1102 (w), 1064 (w), 1037 (w), 1018 (w), 957 (w), 898 (w), 878 (w), 837 (w), 813 (w), 774 (w), 730 (w), 713 (w), 702 (w), 640 (w), 585∼602 (w), 532 (w) cm^{-1}. Mass: 269 $[C_5F_{11}^+]$, 219 $[C_4F_9^+]$, 143 $[C_4F_5^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 69 $[CF_3^+]$, 47 $[C(O)F^+]$. Physical properties and analytical data of 5d, and its ^{19}F nmr data are shown in Tables 2 and 6 respectively.

Fluorination of 9

Similarly, 9 (13.7 g, 0.087 mol) was fluorinated under the following cinditions; 3.5 A/dm^2, 5.8~8.5 V, 5~6 °C, 227 min (125 Ahr). The products weighed 8.3 g for those collected at cold traps and 7.2 g for cell drainings respectively. The products obtained from cold traps were worked up similar to that explained for 1a. Thus, the following compounds were obtained; The less volatile compounds, 6.5 g, 13 (0.3), 14 (2.0), 15 (0.2), 16 + 17 (0.7), 20 (0.2), 21 (1.9), unidentified (1.3). Cell drainings, 7.2 g, 5e (5.0), unidentified (2.2). Perfluoro-(n-butyl n-hexylether) (5e)(nc): IR: 1336 (m), 1304 (ms), 1251 (vs), 1231 (s,sh), 1196 (s,sh), 1159 (s), 1132 (ms), 1099 (m), 1066 (w), 988 (w), 955 (w), 899 (m), 856 (w), 816 (w), 770 (w), 741 (m), 718 (m), 658 (w), 533 (w) cm^{-1}. Mass: 319 [$C_6F_{13}^+$], 231 [$C_5F_9^+$], 219 [$C_4F_5^+$], 181 [$C_4F_7^+$], 169 [$C_3F_7^+$], 131 [$C_3F_5^+$], 119 [$C_2F_5^+$], 100 [$C_2F_4^+$], 69 [CF_3^+]. Physical properties and analytical data of 5e and its ^{19}F nmr data are shown in Tables 2 and 6 respectively.

§ Purification of perfluoro(2-alkyloxolane)s

The reaction of a mixture of 2a and 3a with anhydrous $AlCl_3$ at various temperatures

As typical examples, the reactions carried out under the following reaction conditions will be described.

1) at 150 °C for 20 hrs

A reaction mixture of perfluorocyclic ethers (PCE)(2a/3a = 1 : 0.149)(1.80 g, 4.93 mmol) and an two molar excess of $AlCl_3$ (1.3 g) was held in a 30 ml Hoke bomb at 150 °C for 20 hrs. The products were subjected to fractional condensation using traps at -196 °C and -78 °C. The low bps compounds in the trap at -196 °C were primarily HCl and small amounts of $COCl_2$. The compounds in the trap at -78 °C were found to consist of an unreacted PCE (1.37 g), and trace amounts of C_2Cl_6 and 6a by GLC analysis (Col. D). The ^{19}F nmr analysis of an unreacted PCE showed that it still contained small amounts of 3a (2a/3a = 1 : 0.046).

2) at 150 °C for 46 hrs

Similarly, the reaction was carried out using the following reaction mixture (PCE, 1.87 g, 4.87 mmol; $AlCl_3$, 1.30 g) under the same reaction temperature (150 °C) but for the prolonged reaction time (46 hrs). The products were worked up similarly. Thus, the following compounds were collected at -78 °C trap; PCE (0.98 g), C_2Cl_6 (0.13 g), 6a (0.18 g, 0.44 mmol), 7a (0.60 g, 0.38 mmol). The ^{19}F nmr spectrum of an unreacted PCE revealed that it is pure 2a. These new compounds (2a, 6a and 7a) were isolated by semi-preparative GLC (Col. H), and were characterized spectroscopically. Perfluoro(2-ethyloxane) (2a)(nc): IR: 1356 (m), 1342 (m), 1285 (ms), 1246 (vs), 1216 (vs), 1155 (s), 1125 (m,sh), 1096 (ms), 1079 (s), 1037 (m), 1015 (w), 964 (ms), 859 (w), 833 (ms), 748 (ms), 716 (w), 644 (m), 618 (m), 594 (w), 554 (w), 541 (w), 512 (m), 336 (w) cm^{-1}. Mass: 345 $[M-F]^+$, 247 $[M-C_2F_5]^+$, 231 $[C_2F_9^+]$, 219 $[C_4F_9^+]$, 181 $[C_4F_8^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 100 $[C_2F_4^+]$, 69 $[CF_3^+]$. Perfluoro(2,5,5-trichloro-2-n-propyloxolane) (6a)(nc): IR (film): 1349 (ms), 1325 (s), 1284 (ms), 1190∼1254 (vs), 1128 (s), 1070 (ms), 1041 (s), 1021 (s), 974 (ms), 951 (ms), 922 (ms), 904 (ms), 881 (s), 857 (m), 807 (ms), 782 (m), 775 (m), 743 (ms), 737 (m), 722 (ms), 715 (ms), 690 (w), 663 (m), 642 (w), 610 (w), 592 (w), 551 (w), 534 (w), 492 (w) cm^{-1}. Mass: 397 $[M-Cl^{35}]^+$, 245 $[M-C_3F_7]^+$, 85 $[CF_2Cl^{35}]^+$, 69 $[CF_3^+]$ (The chlorine isotope ratio was consistent with ion assignment, but the Cl^{37}ions have been omitted). Perfluoro(5,5-dichloroheptanoyl chloride) (7a)(nc): IR (film): 1787 ($\nu_{C=O}$) (ms), 1355 (m), 1328 (m), 1313 (m), 1290 (m), 1230∼1235 (vs), 1192 (vs), 1161 (s,sh), 1130 (s), 1118 (ms), 1080 (ms), 1055 (ms), 1061 (m), 942 963 (w,broad), 920∼927 (w), 851 (w), 816 (w), 795 (w), 781 (w), 761 (w), 745 (w), 731 (w), 722 (ms), 711 (m), 694 (w), 670 (w), 630 (w), 620 (w), 608 (w), 532 (w) cm^{-1}. Mass: 379 $[M-Cl^{35}]^+$, 267 $[C_4F_6Cl_3^{35+}]$, 147 $[C_3F_5O^+]$, 119 $[C_2F_5^+]$, 69 $[CF_3^+]$. Physical properties and analytical data of 2a, and those of 6a and 7a are shown in Tables 2 and 5 respectively. The ^{19}F nmr data of 2a and 6a, and those of 7a are presented in Fig. 1 and Table 6 respectively.

Several other reactions carried out under the similar conditions but at the reaction temperatures of 160 °C, 170 °C and

190 °C respectively are summarized in Table 3 together with those explained above.

Reaction of a mixture of 2f and 3f with anhydrous $AlCl_3$

In a 30 ml Hoke bomb, a mixture of 2f and 3f (2f/3f = 1 : 0.326, 1.6 g, 5.36 mmo$l$) was condensed onto the granular $AlCl_3$ (1.4 g) and kept at 155 °C for 30 hrs. The products were subjected to fractional condensation using traps at -98 °C and -196 °C. The low bps compounds in the trap at -196 °C were primarily $COCl_2$ and small amounts of Cl_2 and HCl. Gas chromatographic separation (Col. C,D) of the products at -98 °C yielded the following compounds; pure 2f (by IR spectroscopy) [4,7] (0.80 g, 2.54 mmo$l$), CCl_4 (0.15 g), C_2Cl_6 (trace), 6f [4,7] (0.38 g, 1.08 mmo$l$). The compounds which remained in the bomb were rinsed out with small amounts of Daiflon S3 solvent several times. After the green powder had been filtered off, the majority of the solvent was removed off to give a liquid (0.6 g) by using a rotary evaporator. Its GLC analysis (Col. D) showed only the presence of small amounts of C_6Cl_6 other than a solvent.

Reaction of a mixture of 2b and 3b with anhydrous $AlCl_3$

Similarly, a reaction mixture of PCE (2b/3b = 1 : 0.364, 1.76 g, 4.23 mmo$l$) and $AlCl_3$ (1.2 g) in a 30 ml Hoke bomb was kept at 155 °C for 46 hrs. The products were subjected to fractional condensation using traps at -196 °C and -78 °C. The products at -196 °C were primarily HCl and small amounts of $COCl_2$. The compounds in the trap at -78 °C were primarily unreacted PCE (0.94 g) and small amounts of CCl_4 and 6b by GLC analysis (Col. D). The ^{19}F nmr spectrum of an unreacted PCE revealed that it is a pure 2b. The compounds which retained in the Hoke bomb were worked up in a manner similar to that described for the reaction of a mixture of 2f and 3f. GLC analysis of the liquid yielded 6b [4,7] (0.31 g, 0.66 mmo$l$), 7b (0.13 g, 0.28 mmo$l$) and C_6Cl_6 (trace). Perfluoro(2-n-propyloxane) (2b)(nc): IR: 1356 (m), 1333 (ms), 1319 (ms,sh), 1281 (s), 1251 (vs), 1203∼1226 (vs), 1186 (ms,sh), 1155 (s), 1132 (ms), 1113 (ms), 1100 (ms), 1076 (m,sh), 1054 (s), 1026 (w), 999 (ms), 986 (m,sh), 956 (m), 933 (m), 942 (w), 819 (m), 803 (ms), 751 (m,sh), 739 (ms), 714 (m), 676 (w), 643 (m), 616 (m), 596 (w), 556 (w), 535 (w), 518 (w), 501 (w) cm^{-1}. Mass: 397 $[M-F]^+$, 219 $[C_4F_9{}^+]$, 169 $[C_3F_7{}^+]$, 131 $[C_3F_5{}^+]$, 119 $[C_2F_5{}^+]$, 100 $[C_2F_4{}^+]$, 69 $[CF_3{}^+]$. Perfluoro(2,5,5-trichloro-2-n-butyloxolane) (6b)[4,7]: IR (film): 1395 (w), 1355 (m), 1327 (s), 1295 (m,sh), 1235 (vs), 1208 (vs), 1193 (s,sh), 1142 (s), 1090 (m,sh), 1090 (m,sh), 1062 (ms), 1048 (s), 1020 (s), 982 (w), 910～938 (ms), 877 (s), 857 (m,sh), 841 (ms), 801 (m), 793 (ms), 763 (w), 751 (w), 743 (w), 736 (w), 711 (m), 692 (m), 670 (m), 633 (w), 587 (w), 553 (w), 537 (w), 518 (w) cm^{-1}. Mass: 429 $[M-Cl^{35}]^+$, 245 $[M-C_4F_9]^+$, 69 $[CF_3{}^+]$. Perfluoro(5,5-dichloro-octanoyl chloride) (7b)(nc): IR (film): 1784 ($\nu_{C=O}$) (m), 1346 (ms), 1316 (m), 1294 (m,sh), 1236 (vs), 1197 (vs), 1196 (s,sh), 1160 (ms,sh), 1132 (ms), 1113 (m,sh), 1079 (ms), 1014 (m,sh), 1007 (m), 984 (w,sh), 944 (w), 913 (w), 879 (w,sh), 846 (ms), 804 (w), 789 (w), 754 (w), 729 (w), 711 (m), 694 (w), 669 (w), 625 (w) cm^{-1}. Mass: 429 $[M-Cl^{35}]^+$, 267 $[C_4F_6Cl_3^{35+}]$, 169 $[C_3F_7{}^+]$, 69 $[CF_3{}^+]$. Physical properties and analytical data of 2b, and those of 6b and 7b are shown in Tables 2 and 3, respectively. ^{19}F nmr data of 2b and 6b, and those of 7b are presented in Fig. 1 and Table 6 respectively.

Reaction of a mixture of 2c and 3c with anhydrous $AlCl_3$

Similarly, a reaction mixture of PCE (2c/2b/3b = 1 : 1.279 : 0.259)(5.47 g, 13.14 mmol) and $AlCl_3$ (3.5 g) were kept in a 30 ml Hoke bomb at 160 °C during 40 hrs. The work-up of the products were the same as those explained for the reaction of a mixture of 2b and 3b. However, in this experiment, as a complex mixture of chlorinated products were obtained, no further works to separate them were conducted. Thus, the following compounds were obtained; PCE (1.98 g, 4.8 mmol), chlorinated compounds having an empirical formula $C_8F_{13}Cl_3O$ (by Mass analysis) (2.11 g, 4.53 mmol), C_6Cl_6 (0.22 g). The ^{19}F nmr analysis of an unreacted PCE showed that it consisted of a mixture of 2c and 3c (2c/3c = 1 : 0.870). No attempt to resolve these two isomers by GLC was conducted. The ^{19}F nmr data of 2c are shown in Fig. 1.

Reaction of a mixture of 2d and 3d with anhydrous $AlCl_3$

Similarly, a reaction mixture of PCE (2d/3d = 1 : 0.276) (4.46 g, 9.58 mmol) and $AlCl_3$ (2.6 g) were kept in a 30 ml Hoke bomb at 160 °C for 44 hrs. The work-up of the products was the same as those explained for the reaction of a mixture of 2b and 3b. Thus, the following compounds were obtained; pure 2d (confirmed by ^{19}F nmr analysis)(1.82 g, 3.90 mmol), C_6Cl_6 (0.15 g), 6d (1.09 g, 2.11 mmol), 7d (1.44 g, 2.79 mmol). Perfluoro(2-n-butyloxane) (2d)(nc): IR: 1355 (m), 1332 (ms), 1295 (ms,sh), 1275 (s), 1238∼1250 (vs), 1205∼1215 (s), 1183 (ms,sh), 1154 (s), 1140 (s), 1112 (ms), 1080 (m), 1065 (m), 1052 (m,sh), 1041 (s), 978 (ms), 920 (w), 891 (m), 835 (w), 820 (w,sh), 810 (m), 791 (m), 747 (ms), 731 (ms), 714 (m), 682 (m), 642 (m), 630 (w,sh), 614 (m), 601 (w), 582 (w), 555 (w), 530 (w), 509 (w) cm^{-1}. Mass: 447 $[M-F]^+$, 247 $[M-C_4F_9]^+$, 219 $[C_4F_9^+]$, 131 $[C_3F_5^+]$, 119 $[C_2F_5^+]$, 100 $[C_2F_4^+]$, 69 $[CF_3^+]$. Perfluoro(2,5,5-trichloro-n-amyloxolane) (6d)(nc): IR (film): 1355 (w), 1330 (m), 1242 (vs), 1205 (vs), 1152 (m,sh), 1143 (ms), 1113 (w), 1060 (w,sh), 1041 (m), 1022 (m), 982 995 (w), 902∼925 (w,broad), 885 (w,sh), 872 (m), 815 (m), 798 (w), 773 (w), 652∼744 (w) cm^{-1}. Mass: 479 $[M-Cl^{35}]^+$, 85 $[CF_2Cl^{35+}]$, 69 $[CF_3^+]$. Perfluoro(5,5-dichlorononanoyl chloride) (7d)(nc): IR (film): 1786 ($\nu_{C=O}$) (m), 1356 (m), 1317 (w), 1294 (w,sh), 1244 (vs), 1223 (s,sh), 1194 (s), 1161 (ms), 1143 (s), 1080 (w), 1064 (w), 1017 (w), 964∼984 (w,broad), 932 (w), 851 (ms), 799 (w), 711∼749 (w,broad) cm^{-1}. Mass: 479 $[M-Cl^{35}]^+$, 267 $[C_4F_6Cl_3^{35+}]$, 219 $[C_4F_9^+]$, 69 $[CF_3^+]$. Physical properties and analytical data of 2d, and those of 6d and 7d are shown in Tables 2 and 5, respectively. ^{19}F nmr data of 2d and 6d, and those of 7d are presented in Fig. 1 and Table 6, respectively.

Reaction of a mixture of 2e and 3e with anhydrous $AlCl_3$

Similarly, a reaction mixture of PCE (2e/3e = 1 : 0.152, 2.60 g, 5.58 mmol) and $AlCl_3$ (1.5 g) were held in a 30 ml Hoke bomb at 160 °C for 48 hrs. The products were worked up in a similar manner to that explained for the reaction of a mixture of 2b and 3b. Thus, the following compounds were obtained: pure 2e (confirmed by ^{19}F nmr analysis) (1.33 g, 2.57 mmol), C_2Cl_6 (trace), 6e (0.31 g, 0.55 mmol), 7e (0.52 g, 0.93 mmol). Perfluoro(2-n-amyloxane) (2e)(nc): IR (film): 1380∼1400 (w), 1350 (m), 1333 (m), 1275 (m,sh), 1240 (s), 1205 (vs), 1140∼1150 (ms), 1116 (m), 1090 (w), 1056 (m), 1011 (m), 985 (w), 968 (w), 878 (w), 778∼798 (w), 725∼745 (w), 681 (w), 640 (w), 613 (w), 600 (w) cm^{-1}. Mass: 497 $[M-F]^+$, 247 $[M-C_5F_{11}]^+$, 219 $[C_4F_9{}^+]$, 181 $[C_4F_7{}^+]$, 131 $[C_3F_5{}^+]$, 119 $[C_2F_5{}^+]$, 100 $[C_2F_4{}^+]$, 69 $[CF_3{}^+]$. Perfluoro(2,5,5-trichloro-n-hexyloxolane) (6e)(nc): IR (film): 1375∼1405 (w,broad), 1305∼1335 (m,broad), 1240 (vs), 1203 (vs), 1180 (s,sh), 1158 (ms), 1147 (ms), 1080 (m), 1020 (m) cm^{-1}. Mass: 529 $[M-Cl^{35}]^+$, 85 $[CF_2Cl^{35+}]$, 69 $[CF_3{}^+]$. Perfluoro(5,5-dichlorodecanoyl chloride) (7e)(nc): IR (film): 1785 ($\nu_{C=O}$) (m), 1375∼1405 (w,broad), 1355 (m), 1305∼1320 (m,sh), 1244 (vs), 1207 (vs), 1162 (ms), 1146 (s), 1124 (ms), 1078 (m), 1018 (m), 985 (w), 915∼935 (w,broad), 850 (m), 792 807 (w,broad), 746 (m), 715 735 (m,broad) cm^{-1}. Mass: 529 $[M-Cl^{35}]^+$, 267 $[C_4F_6Cl_3^{35+}]$, 69 $[CF_3{}^+]$. Physical properties and analytical data of 2e, and those of 6e and 7e are shown in Tables 2 and 5 respectively. ^{19}F nmr data of 2e and 6e, and those of 7e are presented in Fig. 1 and Table 6, respectively.

ACKNOWLEDGEMENT

The authors wish to thank Mr. Hitoshi Gyo for able assistance.

REFERENCES

1 For example, Minnesota Mining and Manufacturing Co., U.S. 2,644,823: Brit. 718,318. In this patent, it is stated actually that the perfluoro(2-alkyloxane)s would produce as the main cyclization product by the electrochemical fluorination of the straight-chain carboxylic aicds. However, it it accepted to date that the principal cyclization product is its isomeric perfluoro(2-alkyloxolane)s, but not the stated perfluoro-(2-alkyloxane)s. Our results dealing with the fluorination of aliphatic primary alcohols coincided with these observations, though we missed the presence of the perfluoro(2-alkyloxane)s which might existed in small quantities among the products [T. Abe, S. Nagase and H. Baba, Bull. Chem. Soc. Jpn., 49 (1976) 1888].

2 T. Abe, K. Kodaira, H. Baba and S. Nagase, J. Fluorine Chem., 12 (1978) 1.

3 T. Abe and S. Nagase, J. Fluorine Chem., 13 (1979) 519.

4 T. Abe and S. Nagase, J. Fluorine Chem., 12 (1978) 359.

5 N. I. Shikin, I. F. Bel'skii, R. A. Karakhanov, B. Kozma and M. Bartok, Acta Univ. Szeged., Acta Phys. Chem., 9 (1963) 37: Chem. Abstr., 60 (1964) 4094b.

6 W. G. Young and J. D. Robert, J. Amer. Chem., 77 (1955) 4837.