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THE ELECTROCHEMICAL FLUORINATION OF α-ALKYL-SUBSTITUTED CARBOXYLIC ACIDS*

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SUMMARY

The electrochemical fluorination of acid chlorides and methyl esters of the α-alkyl-substituted carboxylic acids (2-methyl-n-valeryl chloride, 2-methyl-n-caproyl chloride, 2-methyl-n-enanthyl chloride, 2,3-dimethyl-n-buturyl chloride, methyl 2-ethyl-n-valerate, 2-n-propyl-n-valeryl chloride, 2-ethyl-n-caproyl chloride and methyl 2-n-butyl-n-caproate) was conducted to give a series of the substituted perfluorooxolanes and perfluorooxanes as well as the corresponding perfluoroalkanoyl fluorides in good yields. The physical properties of the new compounds obtained are reported together with some of the ^{19}F nmr data.

INTRODUCTION

There is much current interest in perfluoro-compounds, especially in perfluorocyclic ethers, as carriers for oxygen in an artificial blood [1,2]. Polyfluorocyclic ethers have mainly been synthesized not only by the fluorination of cyclic ethers

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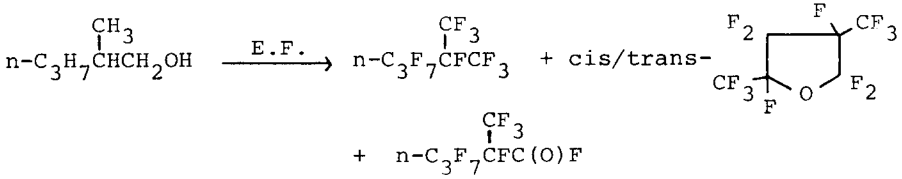
by cobaltic trifluoride [3,4] but also by the electrochemical fluorination of the oxygen containing compounds. The latter method involves the fluorination of carboxylic acids [5-8], alcohols and aldehydes [9] as well as cyclic ethers [10-13]. However, the investigation of the carboxylic acids by the electrochemical fluorination has not extended beyond the straight -chain carboxylic acids [14].

We previously investigated the electrochemical fluorination of alcohols [9] which afforded perfluorocyclic ethers and perfluoroalkanoyl fluorides in fair yields. When such a β-alkyl-substituted alcohol as 2-methyl-1-pentanol was fluorinated, however, major products obtained were perfluorocarbons together with small amounts of the expected perfluorocyclic ethers and a perfluoroalkanoyl fluoride, viz.

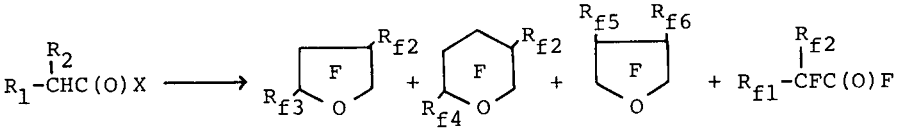


In this connection, it seemed of interest to investigate the fluorination of the α-alkyl-substituted carboxylic acids to obtain various kinds of the perfluoro-(di-alkyl-substituted oxolane)s as the cyclization products.

This paper deals with the synthesis and characterization of a series of the previously unreported substituted perfluoro-oxolanes, perfluorooxanes and perfluoroalkanoyl fluorides which were produced by the electrochemical fluorination of the following eight of the α-alkyl-substituted carboxylic acids; 2-methyl-n-valeryl chloride (1), 2-methyl-n-caproyl chloride (2), 2-methyl-n-enanthyl chloride (3), 2,3-dimethyl-n-butyryl chloride (4), methyl 2-ethyl-n-valerate (5), 2-n-propyl-n-valeryl chloride (6), 2-ethyl-n-caproyl chloride (7), and methyl 2-n-butyl-n-caproate (8). As a result of this investigation, this method is revealed as greatly useful for the preparation of the substituted perfluorocyclic ethers, i.e. perfluoro-2,4-dialkyloxolanes, which had not been accessible. One of the reason for this is because of the synthetic difficulties of making the corresponding cyclic ethers as raw materials.

RESULTS AND DISCUSSION

The electrochemical fluorination of carboxylic acid chlorides dealt in this paper proceeded smoothly except in the case of 2-ethyl-n-valeryl chloride and 2-n-butyl-n-caproyl chloride, which would not pass an electric current because of the formation of tarry material. In such cases, the methyl esters of the parent carboxylic acids (5 and 7) were fluorinated in place of the acid chlorides. The electrochemical fluorination of these α-alkyl-substituted carboxylic acids has been found to yield mainly the perfluorooxolanes and perfluorooxanes as the cyclization products, and the corresponding perfluoroalkanoyl fluorides along with fragmentation products in good yields. The fluorination of α-alkyl-substituted carboxylic acids is represented by the following scheme:



$X=Cl$ for 1-4, 6 and 7
$X=OCH_3$ for 5 and 8

	R_1	R_2	R_{f1}	R_{f2}	R_{f3}	R_{f4}	R_{f5}	R_{f6}
(1)	$n-C_3H_7$	CH_3	$n-C_3F_7$	CF_3	CF_3	F		
(2)	$n-C_4H_9$	CH_3	$n-C_4F_9$	CF_3	C_2F_5	CF_3		
(3)	$n-C_5H_{11}$	CH_3	$n-C_5F_{11}$	CF_3	$n-C_3F_7$	C_2F_5		
(4)	$iso-C_3H_7$	CH_3	$iso-C_3F_7$	CF_3			CF_3	CF_3
(5)	$n-C_3H_7$	C_2H_5	$n-C_3F_7$	C_2F_5	CF_3	F		
				$n-C_3F_7$	F			
(6)	$n-C_3H_7$	$n-C_3H_7$	$n-C_3F_7$	$n-C_3F_7$	CF_3	F		
(7)	$n-C_4H_9$	C_2H_5	$n-C_4F_9$	C_2F_5	C_2F_5			
				$n-C_4F_9$	F			
(8)	$n-C_4H_9$	$n-C_4H_9$	$n-C_4F_9$	$n-C_4F_9$	C_2F_5			

Scheme 1

The reaction conditions for the fluorination and the results obtained are summarized in Tables 1 and 2. Apart from the compounds listed in Table 1, considerable amounts of such perfluoroalkanes as perfluoropentane (from 1 and 4), perfluorohexane (from 2 and 5), perfluoroheptane (from 3, 6 and 7), and

Table 1. Results of the fluorinations of α-alkyl-substituted carboxylic acids

Run No.	Sample (mol)	Electricity passed (Ahr)	Fluorinated compounds obtained (g)	Perfluorocyclic ethers and perfluoroalkanoyl fluorides obtained (Yield %)
I	1 (0.199)	141	38.0[a]	$\overline{\mathrm{CF(CF_3)CF_2CF(CF_3)CF_2O}}$ (9)[c] (19.9), $\overline{\mathrm{CF(CF_3)(CF_2)_4O}}$ (10) (5.5), $\overline{\mathrm{CF_2CF(CF_3)(CF_2)_3O}}$ (11) (10.4), n-$C_3F_7CF(CF_3)C(O)F$ (12) (7.0).
II	2 (0.203)	154	24.5 (1.9)[b]	$\overline{\mathrm{CF(C_2F_5)CF_2CF(CF_3)CF_2O}}$ (13)[d] (8.8), $\overline{\mathrm{CF(CF_3)CF_2CF_2CF(CF_3)CF_2O}}$ (14) (4.0), n-$C_4F_9CF(CF_3)C(O)F$ (15) (3.0).
III	3 (0.188)	186	9.6 (27.2)	$\overline{\mathrm{CF(n\text{-}C_3F_7)CF_2CF(CF_3)CF_2O}}$ (16)[e] (10.5), $\overline{\mathrm{CF(C_2F_5)CF_2CF_2CF(CF_3)CF_2O}}$ (17) (5.0), n-$C_5F_{11}CF(CF_3)C(O)F$ (18) (10.2).
IV	4 (0.201)	157	31.0	9[f] (4.7), $\overline{\mathrm{CF_2CF(CF_3)CF(CF_3)CF_2O}}$ (19) (2.2), $\overline{\mathrm{CF_2C(CF_3)_2CF_2CF_2O}}$ (20) (0.8), 12 (5.1), iso-$C_5F_{11}C(O)F$ (21) + iso-$C_3F_7CF(CF_3)C(O)F$ (22) (6.7).

Table 1. continued:

V	5 (0.244)	254	37.4 (4.2)	$\overline{CF(CF_3)CF_2CF(C_2F_5)CF_2O}$ (23)[g] (10.1), $\overline{CF_2CF_2CF(n\text{-}C_3F_7)CF_2O}$ (24) (4.7), $\overline{CF_2(CF_2)_2CF(C_2F_5)CF_2O}$ (25) (2.4), $n\text{-}C_3F_7CF(C_2F_5)C(O)F$ (26) (9.8).
VI	6 (0.202)	213	16.6 (31.0)	$\overline{CF(CF_3)CF_2CF(n\text{-}C_3F_7)CF_2O}$ (27) (19.9), $\overline{CF_2(CF_2)_2CF(n\text{-}C_3F_7)CF_2O}$ (28) (7.3), $(n\text{-}C_3F_7)_2CFC(O)F$ (29) (6.7).
VII	7 (0.208)	204	18.3 (36.8)	$\overline{CF(C_2F_5)CF_2CF(C_2F_5)CF_2O}$ (30) (17.0), $\overline{CF_2CF_2CF(n\text{-}C_4F_9)CF_2O}$ (31) (14.0), $n\text{-}C_4F_9CF(C_2F_5)CFC(O)F$ (32) (11.5).
VIII	8 (0.202)	283	13.3 (52.9)	$\overline{CF(C_2F_5)CF_2CF(n\text{-}C_4F_9)CF_2O}$ (33) (20.6), $(n\text{-}C_4F_9)_2CFC(O)F$ (34) (12.8).

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a) Product obtained in cold traps. b) Cell drainings in parentheses. c) Cis/trans ratio =1.2. d) Cis/trans ratio=1.3. e) Cis/trans ratio=1.2. f) Cis/trans ratio=0.9. g) Cis/trans ratio=1.4.

Table 2. Perfluorocarboxylic acids obtained from gas washing bottles

Run No.	Na salt of perfluorocarboxylic acids obtained (g)	Composition (mol%)
I	2.3	$CF_3C(O)ONa$ (35) (15), $C_2F_5C(O)ONa$ (36) (20), n-$C_3F_7C(O)ONa$ (37) (9), n-$C_4F_9C(O)ONa$ (38) (56).
II	1.5	35 (30), 36 (37), 37 (11). 38 (22).
III	1.8	35 (39), 36 (38), 37 (14), 38 (9).
IV	9.1	35 (9), 36 (45), 37 (5), 38 (30), iso-$C_5F_{11}C(O)ONa$ (12).
V	1.4	35 (43), 36 (21), 37 (22), 38 (14).
VI	1.7	35 (30), 36 (20), 37 (15), 38 (35).
VII	1.3	35 (36), 36 (27), 37 (21), 38 (16).
VIII	2.2	35 (37), 36 (29), 37 (13), 38 (21).

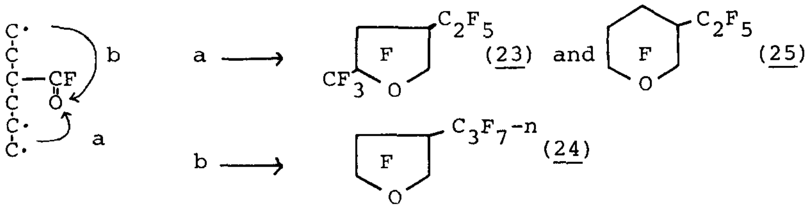
perfluorononane (from 8) were also obtained, which were evidently formed due to decarboxylation of the parent carboxylic acids.

In general, the total yields of the products (excluding the degraded products) ranged from 10-43% based on the amount of the sample charged, and the yields of the perfluorocyclic ethers were slightly higher than those of the perfluoroalkanoyl fluorides throughout Runs.

In the fluorination of 1 (Run I) and 3 (Run III), perfluoro-2,4-dialkyloxolanes and its isomeric perfluoro-2,5-dialkyloxanes were obtained in yields of 11-20% and 5-16%, respectively.

While, the corresponding perfluoroalkanoyl fluorides were obtained in yields of 10-11%. On the other hand, the yields of perfluorocyclic ethers and a perfluoroalkanoyl fluoride obtained from 2 (Run II) were not so good compared with those obtained from 1 and 3. However, their yields remained essentially unchanged despite repeated experiments conducted several times.

In the fluorination of 5 (Run V) and 7 (Run VII), two kinds of perfluorooxolanes and a perfluorooxane were produced besides a perfluoroalkanoyl fluoride, respectively. These carboxylic acids (5 and 7) have two such different alkyl groups as ethyl- and n-propyl- (5), and ethyl- and n-butyl groups (7) on the α-carbon of the acids, respectively. Therefore, there are two ways in intramolecular cyclization for 5 and 7 to form the oxolane ring by use of the two available alkyl groups. For an example, perfluoro-2-methyl-4-ethyloxolane (23) and perfluoro-3-ethyloxane (25), and perfluoro-3-n-propyloxolane (24) obtained from 5 are considered to be formed by the intramolecular cyclization of the acid fluoride by one of the radical attacks toward carbonyl oxygen, alternatively, viz.



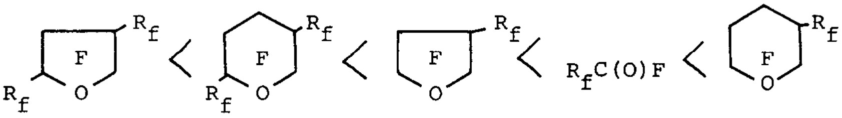
Thus, the expected perfluorooxolanes (perfluoro-2-methyl-4-n-propyloxolane (27) from 6, and perfluoro-2-ethyl-4-n-butyloxolane (33) from 8, respectively) were obtained in good yields from these carboxylic acids as 6 and 8 which had the same alkyl groups (two n-propyl groups for 6, and two n-butyl groups for 8, respectively) on the α-carbon of the acids.

The fluorination of 4 (Run IV) involved extensive rearrangement of the carbon skelton, affording perfluoro-2,4-dimethyloxolane (9), perfluoro-3,4-dimethyloxolane (19) (the expected cyclization product from 4) and perfluoro-3,3-dimethyloxolane (20) [9] as the cyclization products. In addition, considerable amounts of perfluoro-2-methyloxolane [15] (2.8% Yield), perfluoro-3-methyloxolane [9] (3.1%) and perfluorooxane [10,15] (2.0%) were also obtained. Of which, 9 was considered to be formed via cyclization of the 2-methyl-n-valeryl fluoride skelton, an isomerized compound from 4 during fluorination, because perfluoro-2-methyl-n-valeryl fluoride (12) was produced as the principal product. The corresponding perfluoro-2,3-dimethyl-n-butyryl fluoride (22) obtained was found to be mixed with large quantities of perfluoro-iso-valeryl fluoride (21)(40%) as an inseparable constituent, which could be only characterized by means of ^{19}F nmr spectroscopy (Table 3).

Structural determination of the products was carried out on the basis of their spectroscopic data (mass, infrared and ^{19}F nmr), physical properties as well as their elemental analyses (C and F). Among the products obtained, perfluoroalkanoyl fluoride were easily distinguishable from other products both by the carbony absorption in the infrared spectra and by the expected ^{19}F nmr spectra (Table 3).

Although complex ^{19}F nmr spectra were obtained for the substituted perfluorocyclic ethers, the following observations were especially useful for the structural determination of them. 1. the presence of α-difluoromethylene group(s) of the perfluorooxolanes at the lower field which consists of AB pattern [J=130-144 Hz] or complex multiplet at ϕ79-92 ppm. 2. the presence of α-difluoromethylene group(s) of the perfluorooxanes at the lower field which consists of AB pattern [J=158-170 Hz] at ϕ72-94 ppm. 3. the presence of β- and γ-fluoromethin groups of perfluorocyclic ethers (i.e. 3 position of the oxolane ring; 3 and 4 positions of the oxane ring) at ϕ182-189 ppm. 4. the presence of trifluoromethyl group(s) at ϕ71-82 ppm. An exceptional case was the ^{19}F nmr spectrum of 20 obtained from 4, which could be resolved as a first order treatment due to its symmetrical structure (Fig. 1).

Furthermore, the gas chromatogram of the products was also helpful for the determination of the kind of the products. The order of the increasing elution time of the isomeric perfluorocyclic ethers and a perfluoroalkanoyl fluoride in the gas chromatogram (Unit C, Unit D and Unit E, See the experimental section) was found roughly as follows.



Scheme 2

Perfluorooxanes were found to have always slightly higher boiling points, larger refractive indexes and densities than those of isomeric perfluorooxolanes. The physical properties of perfluorocyclic ethers and perfluoroalkanoyl fluorides obtained are shown in Table 4 and 5, respectively.

Among seven kinds of the perfluoro-2,4-dialkyloxolanes synthesized in these experiments, 9, perfluoro-2-ethyl-4-methyloxolane (13) and perfluoro-2-methyl-4-ethyloxolane (23) could be separated with some difficulty into their cis and trans isomers by means of repeated GLC (Unit C, Unit D and Unit E). However, as the perfluoroalkyl groups being attached to the 2 and 4 positions of the oxolane ring become larger, the resolution into their stereoisomers by means of GLC becomes more and more difficult generally. Thus, perfluoro-2-n-propyl-4-methyloxolane (16) could be resolved only incompletely, and the other perfluoro-2,4-dialkyloxolanes like 27, perfluoro-2,4-diethyloxolane (30) and 33 could not be resolved. On the other hand, such perfluoro-2,5-dialkyloxanes as perfluoro-2,5-dimethyloxane (14) and perfluoro-2-ethyl-5-methyloxane (17) obtained from 2 and 3, respectively, 19 obtained from 4, perfluoro-2,3-dimethyloxolane [9], and perfluoro-2,5-dimethyloxolane [16] could not be resolved by GLC at all. Because fluorocarbons are known to have almost identical physical properties with those of their isomers usually, it is difficult to isolate and purify them. One of the notable example of the isolation of the stereoiosmer may be the separation of cis- and trans-perfluorodecalin [17]. As far as the perfluoro-2,4-dialkyloxolanes are concerned, it seemed likely that the substitution of fluorines by the relatively small alkyl groups (CF_3- and C_2F_5 groups) both at the 2- and 4 positions of the oxolane ring caused the large distortion of the molecule so as to be possible to be separated into respective isomers by GLC successfully.

Table 3. ^{19}F nmr and IR data of perfluoroalkanoyl fluorides

Compd	Formula	$\nu_{c=o}$ (cm^{-1})	Chemical shift (ppm)[a] A	B	C	D	E	F	G	-C(O)F	J (Hz)
12	$CF_3CF_2CF_2CF(CF_3)C(O)F$	1892, 1877	81.6	124.6	117.9	180.0	73.0			-32.3	A-C=10.5, A-D=2.4
	A B C D E		t-d	m	m	m	m			m	
15	$CF_3CF_2CF_2CF_2CF(CF_3)C(O)F$	1891, 1875	81.6	126.5	120.9	117.4	180.1	72.7		-32.3	A-C-10.3, A-D=2.6
	A B C D E F		t-d	m	m	m	m	m		m	
18	$CF_3CF_2CF_2CF_2CF_2CF(CF_3)C(O)F$	1892, 1875	81.6	126.8	123.0	120.4	117.1	180.4	72.5	-32.3	A-C=10.4, A-D=2.3
	A B C D E F G		t-t	m	m	m	m	m	m	m	
26	$CF_3CF_2CF_2CF(CF_2CF_3)C(O)F$	1887	80.7	123.8	115.8	178.9	117.5 120.9	80.5		-33.7	A-C=11.0, A-D=2.0, F-D=13.9, E-E'=290
	A B C D E F		t-d	m	m	m	J_{AB}	d		m	
29	$(CF_3CF_2CF_2)_2CFC(O)F$	1887, 1871(sh)	81.4	124.6	116.0	179.0				-33.5	
	A B C D		m	m	m	m				m	
32	$CF_3CF_2CF_2CF_2CF(CF_2CF_3)C(O)F$	1888	81.2	126.8	120.6	115.7	179.0	117.4 120.7	80.7	-33.7	A-C=9.9, G-E=12.9, F-F'=294
	A B C D E F G		t	m	m	m	m	J_{AB}	d	m	
34	$(CF_3CF_2CF_2CF_2)_2CFC(O)F$	1888, 1873	81.6	126.5	120.7	115.4	178.4			-33.6	
	A B C D E		m	m	m	m	m			m	
22	$(CF_3)_2CFCF(CF_3)C(O)F^b$		72.1	176.4	182.1	71.5				-31.9	
	A B C D		m	m	m	m				m	
21	$(CF_3)_2CFCF_2CF_2C(O)F^b$		61.9	176.4	109.7	80.2				-46.1	A-E=17.0 A-C=C-A= 12.0,A-D= D-A=5.9, C-E=17.5
	A B C D		d-t-t	m	sep-d	sep-d				m	

Table 3. continued:

a) ϕ value, to center of peak or multiplet: d=doublet, t=triplet, sep=septet, m=multiplet, J_{AB}=AB pattern. b) Recorded as a mixture of 60% perfluoro-2,4-dimethylvaleryl fluoride and 40% perfluoro-iso-valeryl fluoride. The ir spectrum of this mixture contained strong absorptions at 1893 (sh) and 1878 cm^{-1} due to -C(O)F.

Fig. 1 ^{19}F nmr spectra of 20, cis-9, trans-9, cis-13, trans-13, cis-23, trans-23, cis-16, trans-16, 24, 31, 25 and 28

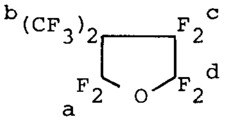
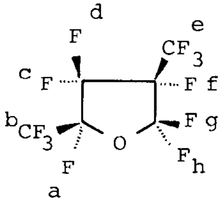
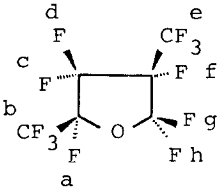
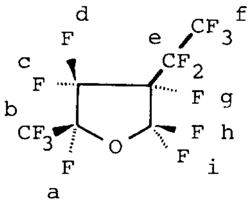
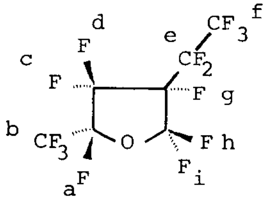
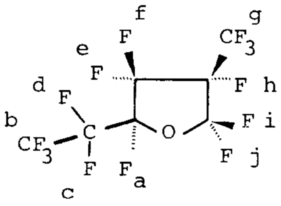
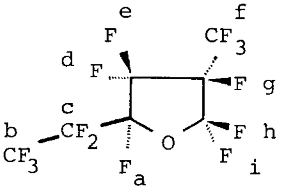
Compd	Formula		Chemical shift[a,b] (ppm)		J (Hz)[b]
20		a	69.9		a-b=b-a=12.9,
		b	63.0		b-c=c-b=12.9,
		c	113.5		b-d=d-b=2.0,
		d	86.4		c-a=a-c=1.9
cis-9		a	124.5		b-d=10.7,
		b	80.1		b-c=3.7,
		c	122.1	J_{AB}	c-d=268
		d	126.4		g-h=140
		e	73.1		
		f	182.3		
		g	73.4	J_{AB}	
		h	182.3		
trans-9		a	127.9		b-c=13.2,
		b	81.3		b-d=2.9,
		c	177.9	J_{AB}	c-d=272,
		d	123.0		g-h=150
		e	74.5		
		f	186.4		
		g	74.1	J_{AB}	
		h	83.6		
cis-23		a	124.9		b-d=12.4,
		b	80.3		b-c=3.6,
		c	121.7	J_{AB}	c-d=270,
		d	126.2		f-g=15.5,
		e	121.2		h-e=248,
		f	81.6		h-g=11.3,
		g	182.3		h-i=142
		h	72.6	J_{AB}	
		i	77.8		

Fig. 1. continued:

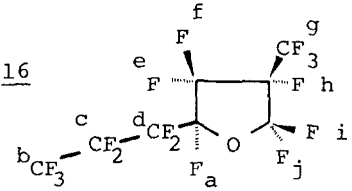
trans-23		a	128.8		c-d=272,
		b	81.7		h-i=142
		c	121.9	J_{AB}	
		d	113.6		
		e	121.4		
		f	81.5		
		g	184.2		
		h	87.2	J_{AB}	
		i	71.7		
cis-13		a	121.6		b-a=12.5,
		b	81.3		b-e=2.6,
		c	122.3	J_{AB}	b-f=2.6,
		d	127.6		c-d=296,
		e	120.8	J_{AB}	e-f=268,
		f	126.1		i-j=144
		g	73.1		
		h	182.3		
		i	75.0	J_{AB}	
		j	78.2		
trans-13		a	126.5		b-a-11.8,
		b	81.2		d-e=266,
		c	123.7		h-i=140
		d	116.0	J_{AB}	
		e	121.9		
		f	74.8		
		g	186.8		
		h	81.9	J_{AB}	
		i	73.5		

a) ϕvalues (ppm relative to internal CCl_3F).

b) Only the evident chemical shifts and coupling constants are given.

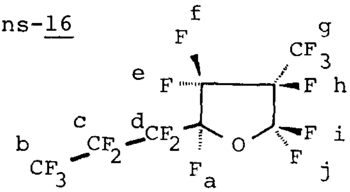
Fig. 1. continued:

cis-16



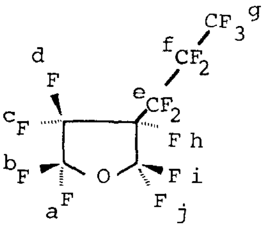
a			b-d=10.2,
b	81.5		b-a=2.5,
c	125.3		g-h=6.8,
d			i-g=14.0,
e			i-h=10.3,
f			i-j=140
g	73.5		
h	182.4		
i	75.6	J_{AB}	
j	79.0		

trans-16



a			b-d=10.2,
b	81.5		b-a=2.6,
c	125.2		e-f=274,
d			i-j=148
e		J_{AB}	
f			
g	74.7		
h	186.6		
i	83.5	J_{AB}	
j	71.7		

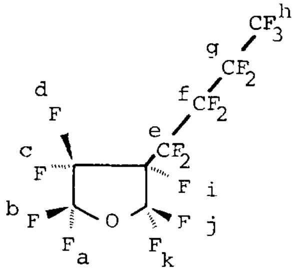
24



a	92.1	J_{AB}	a-b=130,
b	79.8		g-e=10.5,
c,d	125.1		g-h=2.0,
e	117.4		i-h=144
f	125.5		
g	81.2		
h	183.4		
i	73.5	J_{AB}	
j	82.6		

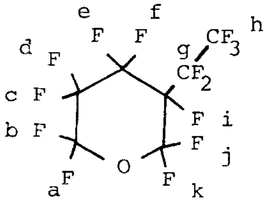
Fig. 1 continued:

31



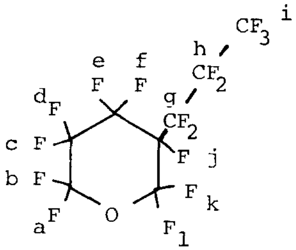
a	92.2	J_{AB}	a-b=132,
b	80.0		h-f=9.9,
c,d	126.0		h-e=2.7,
e	116.9		j-k=142
f	121.8		
g	126.4		
h	81.6		
i	183.4		
j	73.8	J_{AB}	
k	82.6		

25



a	80.9	J_{AB}	a-b=160,
b	93.4		c-d=290,
c	119.2	J_{AB}	e-f=274,
d	130.2		j-k=170
e	125.0	J_{AB}	
f	140.1		
g	117.9		
h	81.4		
i	184.4		
j	72.3	J_{AB}	
k	83.1		

28



a	80.8	J_{AB}	a-b=160,
b	93.2		c-d=298,
c	118.6	J_{AB}	e-f=274,
d	129.1		i-g=12.2,
e	124.7	J_{AB}	k-l=172
f	139.7		
g	114.0		
h	125.6		
i	80.5		
j	183.9		
k	71.8	J_{AB}	
l	79.4		

Table 4. Properties of perfluorocyclic ethers[a]

Compound	Source	BP(°C)[b]	d_4^{20}	Elemental Analysis	
				C(%)	F(%)
cis-9	1,4	50.3- 50.7	1.6844	22.55 (22.79)[c]	72.0 (72.2)
trans-9	1,4	51.1- 51.6	1.6973	22.63 (22.79)	71.9 (72.2)
cis-13	2	74.8- 75.0	1.7386	22.77 (22.95)	72.6 (72.7)
trans-13	2	76.0- 76.4	1.7478	22.61 (22.95)	72.5 (72.7)
cis-23	5	74.5- 75.7	1.7451	22.67 (22.95)	72.5 (72.7)
trans-23	5	75.5- 76.0	1.7488	22.90 (22.95)	72.5 (72.7)
cis-16[d]	3	96.8- 97.3	1.7742	22.98 (23.08)	73.0 (73.1)
trans-16[e]	3	97.8- 98.5	1.7854	22.84 (23.08)	72.9 (73.1)
30[f]	7	98.6- 98.8	1.7800	22.93 (23.08)	73.0 (73.1)
27[g]	6	95.5- 95.7	1.7827	22.90 (23.08)	72.5 (73.1)
33[h]	8	137.0-138.5	1.8325	22.83 (23.26)	72.8 (73.6)
19	4	57.0- 57.6	1.7404	23.01 (22.79)	71.3 (72.2)
24	5	77.3- 77.7	1.7550	22.65 (22.95)	72.5 (72.7)
31[i]	7	102.6-103.1	1.8059	22.89 (23.08)	72.5 (73.1)
25[j]	5	80.0- 80.5	1.7929	22.71 (22.95)	72.7 (72.7)
28[k]	6	107.3-107.8	1.8395	22.86 (23.08)	73.5 (73.1)
14[l]	2	77.5- 78.2	1.7871	22.69 (22.95)	73.0 (72.7)
17[m]	3	99.0- 99.7	1.7963	22.82 (23.08)	72.8 (73.1)

a) All of these are new compounds. b) Boiling points are not corrected. c) Caluculated values in parentheses. d) Contaminated with 23% trans isomer. e) Contaminated with 6%

Table 4. continued:
cis isomer and 8% perfluoro-2-ethyl-5-methyloxane. f) Cis/trans ratio determined by ^{19}F nmr=1.5. g) Cis/trans ratio determined by ^{19}F nmr=1.4. h) Cis/trand ratio determined by ^{19}F nmr=1.4. i) n_D^{20} 1.2830. j) n_D^{20} 1.2812. k) n_D^{20} 1.2881. l) n_D^{20} 1.2794. m) n_D^{20} 1.2816.

There were only very close differences in physical properties between four sets of respective cis and trans isomers of the perfluoro-2,4-dialkyloxolanes [Table 4]. No conclusive clues were obtained from ^{19}F nmr studies on these isomers for distinguishing between them. However, the determination of these isomers was possible by comparison of the physical properties between them with those of the corresponding cis- and trans-perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes. Several kinds of the perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes were prepared by the reaction of the corresponding perfluoro-2,4-dialkyloxolanes with anhydrous aluminum chloride, and were fully characterized [16]. The cis-perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes were found to have slightly lower boiling points, smaller refractive indexes and densities than those of the trans-perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes. These facts lead us to assume that the cis-perfluoro-2,4-dialkyloxolanes had analogously lower boiling points and smaller densities than those of the corresponding trans-perfluoro-2,4-dialkyloxolanes on the basis of the similarlity of the molecular structure between the perfluoro-2,4-dialkyloxolanes and the corresponding perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes. In addition to this, with respect to the chemical shifts of the methin fluorine at the 4 position of the perfluoro-2,5,5-trichloro-2,4-dialkyloxolane, the absorption peaks due to the methin fluorine of the cis form appeared characteristically at a slightly lower field than those found for the trans form. This was consistent with the findings that the absorption peak of the methin fluorine of an isomer of perfluoro-2,4-dialkyloxolane, which was now assigned to cis form because of its lower boiling point and a small density than those of another isomer, was at a slightly lower field (1.7-1.9 ppm) than that found for the trans isomer. Thus in the case of <u>27</u>, <u>30</u> and <u>33</u>, the constituent ratios of stereoisomer were calculated from the areas obtained by integration of the peaks of

Table 5. Properties of perfluoroalkanoyl fluorides[a]

Compound	Source	BP(°C)[b]	d_4^{20}	Elemental Analysis	
				C(%)	F(%)
12	1,4	55.7- 56.2	1.6656	22.70 (22.79)[c]	72.0 (72.2)
15	2	81.0- 81.5	1.7555	22.64 (22.95)	72.5 (72.7)
18[d]	3	102.0-102.8	1.7687	22.55 (23.08)	73.5 (73.1)
26	5	78.0- 78.3	1.7242	22.47 (22.95)	71.9 (72.7)
29[e]	6	99.0-100.0	1.7736	22.78 (23.08)	72.6 (73.1)
32[f]	7	102.1-102.7	1.7688	23.14 (23.08)	72.8 (73.1)
34[g]	8	137.9-138.3	1.8321	22.98 (23.26)	73.5 (73.6)

a) All of these are new compounds. b) Boiling points are not corrected. c) Caluculated values in parentheses. d) n_D^{20} 1.2813. e) n_D^{20} 1.2817. f) n_D^{20} 1.2812. g) n_D^{20} 1.2925.

the methin fluorine in their ^{19}F nmr spectra. The cis/trans ratios of the perfluoro-2,4-dialkyloxolanes, which were determined either by means of GLC or ^{19}F nmr, ranged in an approximate ratio of 1 : 0.7-0.9.

EXPERIMENTAL

Reagents

2-Methyl-n-valeric acid and 2-ethyl-n-caproic acid were purchased from Tokyo Kasei Co.. Other carboxylic acids used were prepared by the malonic acid synthesis in a usual manner; 2-methyl-n-caproic acid, 2-methyl-n-enanthic acid and 2,3-dimethyl-n-butyric acid were prepared by the reaction of the diethyl methylmalonate (Aldrich Chemical Co.) with the corresponding alkyl bromides (Tokyo Kasei Co.). 2-Ethyl-n-valeric acid, 2-n-propyl-n-valeric acid and 2-n-butyl-n-caproic acid were prepared from n-propyl bromide and diethyl ethylmalonate (Tokyo Kasei Co.), n-propyl bromide and diethyl malonate (Tokyo Kasei Co.), and n-butyl bromide and diethyl n-butylmalonate (Tokyo Kasei Co.), respectively. All carboxylic acids so obtained were optically inactive, and were converted into acid chlorides or methyl esters, which were subsequently purified by the fractional distillation before use.

Anhydrous hydrogen fluoride (Daikin Industries Co.) was more than 99.5% pure.

Apparatus

Fluorination was carried out in the usual way [9] using 1*l* electrolytic cell fitted with 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.

A standard Pyrex vacuum line was used in the reaction of cis- and trans-perfluoro-2,4-dimethyloxolanes with anhydrous aluminum chloride for handling the volatile liquids and gaseous materials.

Analytical work was carried out with a Shimadzu GC-2C gas chromatograph using stainless columns (3 mm dia) packed with Silicagel (1.9m)(Unit A), 20% diester of hexamethylene glycol with perfluorocaprylic acid on Chromosorb PAW (6.4 m)(Unit B), 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane on Chromosorb PAW (6.4 m)(Unit C), 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (6.4 m)(Unit D), and 26% Kel F #90 on Chromosorb PAW (3.8 m)(Unit E). 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)(Unit F), 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane on Chromosorb PAW (4.9 m)(Unit G), 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (4.9 m)(Unit H), and 30% Fluorolube HG 1200 on Chromosorb PAW (4.1 m)(Unit I). The carrier gas was helium in all cases.

Infrared spectra were measured on a Hitachi EPI-G3 spectrometer, using a 6 cm gas cell with KBr windows. ^{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.

General procedures for the electrochemical fluorination of the α-alkyl-substituted carboxylic acids

As typical examples of the fluorination of carboxylic acids, the fluorination of 2-methyl-n-valeryl chloride (1) and 2-n-propyl-n-valeryl chloride (6) will be described.

Fluorination of 1 (Run I)

A 26.8 g portion of 1 was dissolved in 1*l* anhydrous hydrogen fluoride in a cell. The evolution of gas (presumed to be HCl) was observed. Then the electrolysis was carried out with an anodic current density of 3.5 A/dm^2, a cell temperature of 5-6 °C, and a cell voltage of 6.4-6.8 V. He (ca. 100 m*l*/min) was bubbled from the bottom of the cell in order to agitate the electrolyte during fluorination. The operation was continued until the voltage reached 10 V. The total quantity of electricity passed was 141 Ahr over 250 min.

The effuluent gases from the cell were passed over NaF pellets and then bubbled through two consecutive bottles containing water (for collection of the perfluorocarboxylic acids which were formed as a result of the hydrolysis of the perfluoroalkannoyl fluorides). The gaseous products which did not react with water were further guided into an alkaline solution of potassium sulfite, and finally collected in traps immersed in liq. nitrogen.

(A) Analysis of the product collected in cold traps

The product collected in cold traps was initially separated into two fractions by using the traps of low temperature distillation unit; Fraction 1 (bp < room temp., 1.3 g) and Fraction 2 (21.5 m*l*, 38.0 g). The fraction 1 consisted of CF_4 (70 mo*l*%), C_2F_6 (22%) and C_3F_8 (8%)(compositions were caluculated on the basis of chromatographic peak areas, assuming equal sensitivities for all components; Unit A, 100 °C). The Fraction 2, shown by

GLC (Unit C, 32 °C) to contain at least 15 components, was carefully distilled using small scale fractional distillation unit to collect the volatile compounds which had the boiling points up to ca. 50 °C. The distillate (1.0 ml, 1.1 g) collected in an ice trap consisted of n-C_5F_{12} (79 mo$l$%) and iso-C_5F_{12} (21%). The distillation residue (17.3 ml, 29.2 g) was further analyzed by GLC (Unit C) to contain the following 5 major and 3 minor compounds (arranged in order of the elution time).

No.	Compound	g
1	not identified	0.6
2	compound A	6.8
3	compound B	5.8
4	perfluoro-2-methyloxane (10)	3.5
5	not identified	1.2
6	n-$C_3F_7CF(CF_3)C(O)F$ (12)	4.4
7	perfluoro-3-methyloxane (11)	6.5
8	perfluorooxepane	0.5

A portion of the distillation residue was isolated by semi-preparative GLC (Unit F and Unit G) to give the individual compounds, which were subsequently characterized spectroscopically.

The 2nd and 3rd compounds (designated compound A and compound B, respectively) had the very similar physical properties with each other. However, the compound B had a slightly higher boiling point (51.5-51.6 °C) and a larger density (d_4^{20} 1.6973) than those (bp 50.3-50.7 °C; d_4^{20} 1.6844) of the compound A. The ^{19}F nmr spectra both of compound A and compound B represented clearly the presence of two kinds of CF_3-groups, one CF-group (being not adjacent to oxygen), and two kinds of CF_2-groups (one being adjacent, and another not adjacent to oxygen), respectively. In their mass spectra, as the largest ion, mass number 297 which was assigned to $[M-F]^+$ ion was observed. The assignment of perfluoro-2,3-dimethyloxolane to one of these was precluded, as this compound was characterized previously in our laboratory [9]. Thus, we concluded that the compound A and the compound B should be the stereoisomers of perfluoro-2,4-dimethyloxolane (9).

Next, in order to confirm the supposed structure of these two compounds, both compound A and compound B were treated with anhydrous aluminum chloride, respectively, to give the corresponding perfluoro-α,α',α'-trichlorooxolanes according to the procedure described previously [9].

The reaction of compound A with $AlCl_3$

The compound A (2.6 g) and granular $AlCl_3$ (1.6 g) were kept in a 30 ml Hoke bomb at 150 °C during 16 hrs to give a clear liquid product (1.7 g), which was analyzed by a combination of trap-to-trap distillation (-78 °C) and GLC (Unit E, 100 °C) to contain unchanged compound A, and two major products (0.7 g) in the ratio of 1 : 0.8. These products were isolated by GLC (Unit I) and were identified on the basis of their spectral data and elemental analysis as cis-perfluoro-2,5,5-trichloro-2,4-dimethyloxolane (cis-39) (22.0% Yield) and trans-perfluoro-2,5,5-trichloro-2,4-dimethyloxolane (trans-39) (16.8%), respectively. The detailed spectral data of several kinds of the perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes including cis-39 and trans-39 will be published in a subsequent paper.

Cis-perfluoro-2,5,5-trichloro-2,4-dimethyloxolane (cis-39) (nc) had bp 130.5-131.5 °C, d_4^{20} 1.7856 and n_D^{20} 1.3607. Found: C, 19.68; F, 46.3%. $C_6F_9Cl_3$ requires C, 19.70; F, 46.8%.

Trans-perfluoro-2,5,5-trichloro-2,4-dimethyloxolane (trans-39) (nc) had bp 131.5-132.3 °C, d_4^{20} 1.7974 and n_D^{20} 1.3613. Found: C, 19.55; F, 46.0%. $C_6F_9Cl_3$ requires C, 19.70; F, 46.8%.

The reaction of compound B with $AlCl_3$

The compound B (2.2 g) was treated with $AlCl_3$ (1.6 g) in the manner described above to give a liquid product (1.6 g) which was shown by GLC to contain two compounds in the ratio of 1 : 0.6 other than the compound B unchanged. These products were found to be cis-39 (38.0% Yield) and trans-39 (21.0%), respectively, on the basis of their identical spectroscopic data (mass, ir and ^{19}F nmr) with those of the authentic samples.

Thus, on the basis of the differences of the physical properties between the compound A and the compound B, it was determined that the former was cis- and the latter was trans-perfluoro-2,4-dimethyloxolanes, respectively.

Cis-perfluoro-2,4-dimethyloxolane (cis-9) (nc): its ir spectrum had absorption bands at 1373 (w), 1351 (m), 1307-1317 (s), 1277 (s), 1252 (sh)(m), 1232 (s), 1182 (s), 1167 (sh)(m), 1110 (vs), 1030 (m), 992 (m), 852 (m), 752 (w), 729 (m), 687 (w) and 579 (w) cm^{-1}. The mass spectrum had the top mass peak at 297 [$C_6F_{11}O^+$], and major mass peaks at 219 [$C_4F_9^+$], 181 [$C_4F_7^+$], 150 [$C_3F_6^+$], 131 [$C_3F_5^+$], 100 [$C_2F_4^+$] and 69 [CF_3^+].

Trans-perfluoro-2,4-dimethyloxolane (trans-9) (nc): its ir spectrum had absorption bands at 1368 (m), 1348 (sh)(m), 1303 (s), 1283 (s), 1243 (vs), 1213 (m), 1158-1185 (broad)(m), 1110 (vs), 1013 (sh)(m), 991 (m), 970 (s), 731 (s), 688 (w) and 596 (w). The mass spectrum had the top mass peak at 297 [$C_6F_{11}O^+$], and the same mass peaks as those found for cis-9.

Results of the elemental analyses, and the ^{19}F nmr spectra of cis-9 and trans-9 are shown in Table 3 and Fig. 1, respectively.

(B) Analysis of the perfluorocarboxylic acids obtained in gas washing bottles containing water

Only such degraded perfluorocarboxylic acids as trifluoroacetic acid (its Na salt-35),perfluoropropionic acid (Na salt-36), perfluorobutyric acid (Na salt-37) and perfluorovaleric acid (Na salt-38) were obtained in this trap. The volatile perfluoro-α-alkyl-substituted alkanoyl fluorides did not react apparently with water, passing through washing bottles safely, and finally condensed in cold traps together with other products.

The acids thus formed were worked up to give sodium salt (2.4 g) by the method described previously [9] and were analyzed by ^{19}F nmr spectroscopy. The ^{19}F nmr sample was made up as saturated ethanol solution of sodium salt of acids. On the basis of the area of the absorptions due to CF_3-groups of the acids, the following composition was determined: 35 (15 mol%), 37+38 (65%), 36 (20%). The mixture of 37 and 38, of which absorptions of CF_3-groups were overlapped (ϕ81.5 ppm), was further analyzed by the integration of each of the α-CF_2 groups (ϕ118.5 ppm for 36 and ϕ117.6 ppm for 37, respectively). Thus, the sodium salt of the acids was found to consist of 35 (15 mol%), 36 (20%), 37 (9%) and 38 (56%).

Fluorination of 6 (Run VI)

The sample 6 (32.4 g) was fluorinated in the manner described above during 214 min until the voltage reached 10 V. The product (16.6 g) trapped in cold traps was analogously worked up to the fluorination of 1 (Run I), and was analyzed by GLC (Unit D, 80 °C) to contain 4 major components. Cell drainings (31.0 g, 17.3 mℓ) was also obtained from the bottom of the cell after the completion of the electrolysis, which was subsequently shaked with a small protion of Molecular Sieves 5A before analysis. The product obtained from the cold traps and the cell drainings, examined by GLC (Unit D, 80 °C) to contain 4 major components, were separated by semi-preparative GLC (Unit F and Unit H). The individual compounds purified were characterized spectroscopically. Thus, the following compounds were obtained.

No.	Compound	g
1	perfluoroheptane	6.4
2	perfluoro-2-methyl-4-n-propyloxolane (27)	16.6
3	$(n\text{-}C_3F_7)_2CFC(O)F$ (29)	5.6
4	perfluoro-3-n-propyloxane (28)	6.1

The physical properties of 27 and 28, and those of 29 are shown in Tables 3 and 4, respectively. ^{19}F nmr spectra of several kinds of perfluorocyclic ethers including 27 and 28, and those of perfluoroalkanoyl fluorides synthesized in these experiments are shown in Fig. 1 and Table 5, respectively. Based on the relative areas of the CF- resonance peaks of a cis and trans mixture of 27, the cis : trans ratio was 1 : 0.7.

The perfluorocarboxylic acids obtained in gas washing bottles were worked up as explained in Run I to yeild 1.7 g of sodium salt, which was found to consist of 35 (30 molℓ%), 36 (20%), 37 (15%) and 38 (35%).

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