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THE REACTION OF PERFLUORO-2,4-DIALKYLOXOLANES WITH ANHYDROUS ALUMINUM CHLORIDE

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SUMMARY

Several kinds of perfluoro-2,4-dialkyloxolanes (A), having such alkyl groups as $R_f=R_f'=CF_3$ (2a); $R_f=C_2F_5$, $R_f'=CF_3$ (3a); $R_f=CF_3$, $R_f'=C_2F_5$ (4a); $R_f=R_f'=C_2F_5$ (5a); $R_f=CF_3$, $R_f'=n-C_3F_7$ (6a) on the 2 and 4 positions of the oxolane ring, respectively, were treated with $AlCl_3$ in a heterogeneous reaction to give the corresponding perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes (B). For purposes of comparison, the respective reactions of perfluoro-2-methyloxolane (1a), perfluoro-2-n-butyloxolane (7a), and perfluoro-2,5-dimethyloxolane (8a) with $AlCl_3$ were also conducted. An increasingly higher reaction temperature was needed for the reaction of A with $AlCl_3$ to give B as the carbon number of A increased. Cis- and trans-perfluoro-4-chloro-2,4-dimethyl-γ-butyrolactones (2c) were obtained from the hydrolytic reactions of cis- and trans-perfluoro-2,5,5-trichloro-2,4-dimethyloxolanes (2b), respectively, with fuming H_2SO_4. Physical properties and ^{19}F nmr data are given for these new compounds.

INTRODUCTION

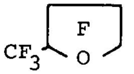
Perfluorocyclic ethers are very stable with regard to thermolysis (~300 °C) and reactions with ordinary chemicals under vigorous conditions, thus providing useful materials for applications which require thermal and oxidative stability. However, as an exception, it has been shown by Tiers [1,2] that perfluorooxolanes with or without a perfluoroalkyl group at the

2 position of the oxolane ring would react with such a Lewis acid as $AlCl_3$ to give the corresponding perfluoro-2,5,5-trichloro-2-alkyloxolanes, or ω,ω,ω-trichlorotetrafluorobutyryl chloride. Recently, the reaction of perfluorooxolanes having, for example, perfluoro-2-oxa-n-hexyl-, perfluoromorpholino-, and perfluoropyridino-groups at the 2 position of the oxolane with $AlCl_3$ was investigated by Kolenko and Ryabinin [3]. However, the expected perfluoro-α,α,α'-trichlorooxolanes were not obtained in these experiments.

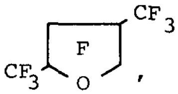
In the preceding paper [4], we described the electrochemical fluorination of α-alkyl-substituted carboxylic acids which afford the perfluoro-2,4-dialkyloxolanes as the anticipated cyclization products as well as perfluoroalkanoyl fluorides in good yields.

The reaction of some of these perfluoro-2,4-dialkyloxolane (A) with $AlCl_3$ is now investigated. One of the purposes of this investigation was to confirm the structure of the starting A, especially in the case where A(2a-4a) could be separated into its respective stereoisomers by GLC, by examining the chlorinated product (B) which were obtained from each of the cis and trans isomers.

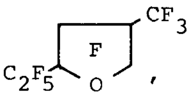
The perfluoro-2,4-dialkyloxolanes (A) used in this investigati were perfluoro-2,4-dimethyloxolane (2a), perfluoro-2-ethyl-4-methyloxolane (3a), perfluoro-2-methyl-4-ethyloxolane (4a), perfluoro-2,4-diethyloxolane (5a), and perfluoro-2-methyl-4-n-propyloxolane (6a). For purposes of comparison, the reaction of such ethers as perfluoro-2-methyloxolane (1a), perfluoro-2-n-butyloxolane (7a), and perfluoro-2,5-dimethyloxolane (8a) with $AlCl_3$ was also attempted.



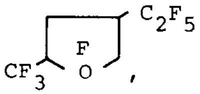
1a



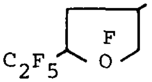
2a



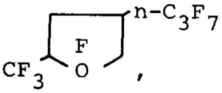
3a



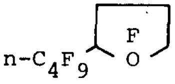
4a



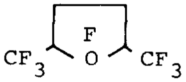
5a



6a



7a



8a

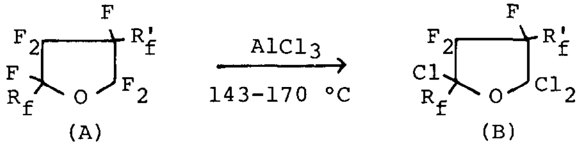
In the case of 2a, 3a, and 4a, the reactions with $AlCl_3$ of pure cis, pure trans, and a mixture of cis and trans isomers were also investigated.

Although perfluoro-2,5,5-trichloro-2-methyloxolane (1b)[1], perfluoro-2,5,5-trichloro-2-n-butyloxolane (8b)[1,3], and cis- and trans-perfluoro-2,5,5-trichloro-2,4-dimethyloxolanes (2b)[4] are not new compounds, their spectroscopic data have not been reported.

In this paper, we wish to report on the reaction of the perfluorocyclic ethers (A) with $AlCl_3$, some hydrolytic reactions of 1b, cis-2b, and trans-2b with fuming H_2SO_4 to give the corresponding perfluorolactones (C), and also the reaction of 1b with $LiAlH_4$ which afforded 2-H-perfluoro-5,5-dichloro-2-methyloxolane (1d) in a low yield.

RESULTS AND DISCUSSION

Perfluoro-2,4-dialkyloxolanes (A) were found to react in a heterogeneous manner with $AlCl_3$ in the temperature range 143-170 °C, analogous to the reaction reported by Tiers [1,2], affording the corresponding perfluoro-2,5,5-trichloro-2,4-dialkyloxolanes (B) in yields of 35-72%, along with gaseous compounds ($COCl_2$ $C_2F_5C(O)Cl$, etc.), perchloro-compounds (CCl_4, C_2Cl_6, and C_6Cl_6), and a tarry material. As has been pointed out, A (1a and 2a) did not react at all with such weaker Lewis acids as $AlBr_3$ and BCl_3.



1: $R_f=CF_3$, $R_f'=F$, 2: $R_f=R_f'=CF_3$, 3: $R_f=C_2F_5$, $R_f'=CF_3$, 4: $R_f=CF_3$, $R_f'=C_2F_5$, 5: $R_f=R_f'=C_2F_5$, 6: $R_f=CF_3$, $R_f'=n-C_3F_7$, 7: $R_f=n-C_4F_9$, $R_f'=F$.

Scheme 1

However, the yields and purities of B varied markedly with reaction conditions. Among the various reaction parameters, it seemed that the reaction temperature influenced most on the yields of the desired B. Generally, when the temperature utilized was higher than the minimum reaction temperature, large quantities of perchlorinated compounds and a tarry material were produced with concomitant decreases both in the amount of B formed and that of A unchanged, even if the temperature difference was only of the order of 10 °C.

In order to find out the optimum reaction temperature, we attempted initially several reactions using 1a, 2a, 5a, and 8a at various temperatures under comparable conditions; a 1.5-2.0 molar excess of $AlCl_3$ was used and the reaction time was limited to about 20 h (Table 1).

In the reactions of 1a, 2a, and 5a with $AlCl_3$, a higher reaction temperature was needed to get the better yields of the desired B as the perfluoroalkyl groups attached to the 2 and 4

Table 1. Reactions of 1a, 2a, 5a, and 8a with $AlCl_3$ at various temperatures

Reactant (mmol)	Reaction conditions temp(°C)/time(hr)	Product[a] (%)	Sample recovered (mmol)	Others (g)
1a(68.9)[b] $AlCl_3$(178)	143/19	1b(53.3)	25.3	$COCl_2$ (0.9), CCl_4 (0.1), C_2Cl_6 (0.3)
1a(79.0)[b] $AlCl_3$(200)	155/17	1b(35.9)	13.3	$COCl_2$ (1.9), CCl_4 (1.5), C_2Cl_6 (1.7)
2a(29.1)[c,d] $AlCl_3$(73)	145/20	————	26.4	$COCl_2$ (trace), CCl_4 (0.2)
2a(28.2)[c,d] $AlCl_3$(75)	155/18	cis-2b(36.4) trans-2b(25.2)	13.6	$COCl_2$ (trace), CCl_4 (0.3), C_2Cl_6 (0.1)
5a(13.8)[e,f] $AlCl_3$(23)	155/20	cis-5b(trace) trans-5b(trace)	10.8	$C_2F_5C(O)Cl$, $COCl_2$ (trace)
5a(11.6)[e,f] $AlCl_3$(26)	170/20	cis-5b(19.6) trans-5b(15.1)	0.5	$COCl_2$, CCl_4. C_2Cl_6 (trace)
8a(16.3)[f] $AlCl_3$(41)	155/21	————	15.9	————
8a(15.6)[f] $AlCl_3$(41)	170/20	8b(19.5)	13.9	$COCl_2$. CCl_4, C_2Cl_6 (trace)

a) The yields of B were calculated based on the sample consumed. b) A 150 ml Hoke bomb was used. c) Cis/trans ratio determined by GLC = 1 : 1.1. d) A 75 ml Hoke bomb was used. e) Cis/trans ratio determined by ^{19}F nmr = 1 : 0.7. f) A 30 ml Hoke bomb was used.

positions of the oxolane ring became larger (1a→2a→5a). On the other hand, 8a did not react at all with $AlCl_3$, even at 155 °C, a temperature at which 2a was easily converted into the corresponding cis-2b [36.4% Yield] and trans-2b [25.8%]. At 170 °C, 8a reacted with $AlCl_3$ successfully and yielded the expected perfluoro-2,5-dichloro-2,5-dimethyloxolane (8b) in low yield [19.5%]. From these observations, the reaction temperatures 155-157 °C were adopted for 3a and 4a, and 6a and 7a, respectively. All these reactions are summarized in Table 2.

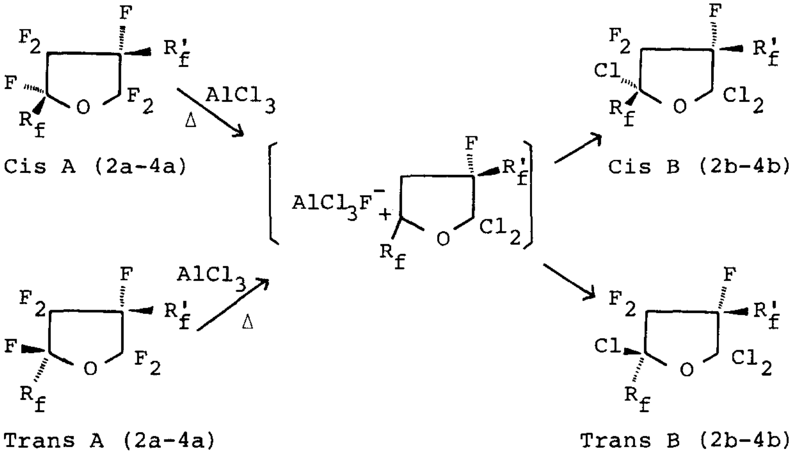
Table 2. Summary of the reactions of perfluorocyclic ethers with $AlCl_3$[a]

Sample (mmol)	Reaction conditions temp(°C)/time(hr)	Product (%)	
1a(68.9)[b,c]	143/17	1b(53.3)	
2a(28.2)[c,d,e]	155/18	cis-2b(36.4),	trans-2b(25.2)
cis-2a(8.1)	155/18	cis-2b(22.2),	trans-2b(16.8)
trans-2a(6.8)	150/17	cis-2b(38.0),	trans-2b(21.0)
3a(8.9)[f]	156/25	cis-3b(26.0),	trans-3b(15.8)
cis-3a(4.8)	156/20	cis-3b(39.1),	trans-3b(25.3)
trans-3a(4.7)	156/19	cis-3b(39.9),	trans-3b(10.3)
4a(9.2)[g]	155/17	cis-4b(40.6),	trans-4b(31.9)
cis-4a(4.8)	156/18	cis-4b(39.8),	trans-4b(31.7)
trans-4a(3.7)	156/18	cis-4b(33.3),	trans-4b(28.8)
5a(11.6)[c,h]	170/21	cis-5b(19.6),	trans-5b(15.5)
6a(13.4)[i]	170/21	cis-6b(26.9),	trans-6b(23.4)
7a(20.2)	170/20	7b(59.6)	
8a(15.3)	175/48	8b(30.5)	

a) An 2-3 molar excess of $AlCl_3$ was used, and a 30 ml Hoke bomb was employed throughout the experiments unless otherwise stated. b) A 150 ml Hoke bomb was used. c) This datum is duplicated with that given in Table 1. d) Cis/trans ratio determined by GLC = 1 : 1.1. e) A 75 ml Hoke bomb was used. f) Cis/trans ratio determined by GLC = 1 : 1.2. g) Cis/trans ratio determined by GLC = 1 : 0.7. h) Cis/trans ratio determined by ^{19}F nmr = 1 : 0.7. i) Cis/trans ratio determined by ^{19}F nmr = 1 : 0.7.

For such compounds as 2a, 3a, and 4a, pure cis, pure trans, and a mixture of cis and trans isomers were also treated with $AlCl_3$, and the products obtained in these reactions were found to consist of cis and trans isomers of B (2b, 3b and 4b) in the approximate ratio 1 : 0.6-0.9, irrespective of the kind of stereoisomers of A used.

The mechanism of this type of halogen exchange reaction has been postulated by Tiers [1] to proceed via a carbonium ion intermediate which formed by abstraction of fluorine by $AlCl_3$ from the α-carbon to the oxygen. Recently, this mechanism was strongly supported by Tatlow and co-workers [5] who observed isomerization as well as replacement in the reaction of enantiomeric halogenated ethers with $AlCl_3$. However, the results obtained in our experiments also definitely explain the participation of the carbonium ion intermediate as is illustrated in Scheme 2.



Scheme 2

The products B (2b-6b) could be separated relative with ease into pure cis and trans isomers by GLC. In contrast, careful gas chromatographic analysis of 8b indicated no sign of the possibility of its separation into cis and trans isomers. This was analogous to the difficulty experienced in an attempted purification of the starting 8a into cis and trans isomers, which remained unresolved by GLC.

Structural determination of these products was carried out on the basis of their ^{19}F nmr, mass, and infrared spectral data as well as their elemental analyses.

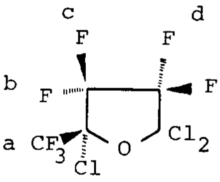
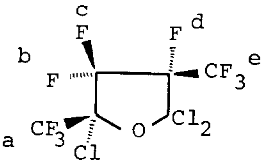
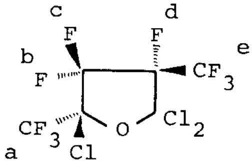
The physical properties and ^{19}F nmr data of these compounds (B) are shown in Table 3 and Fig. 1, respectively. However, only obvious chemical shifts of the chemically non-equivalent nuclei and coupling constants are given in Fig. 1, except those obtained for 1b, cis-2b, and trans-2b.

Table 3. Properties and analytical data of chlorinated perfluorocyclic ethers[a]

Compound	BP(°C)[b]	n_D^{20}	d_4^{20}	Elemental analysis C(%)	Elemental analysis F(%)
1b [c]	103.0-103.5	1.3626	1.7376	19.39 (19.02)[d]	
cis-2b	130.5-131.5	1.3607	1.7856	19.68 (19.70)	46.3 (46.8)
trans-2b	131.5-132.5	1.3613	1.7974	19.55 (19.70)	46.0 (46.8)
cis-3b	147.0-147.5	1.3571	1.8164	20.28 (20.22)	50.2 (50.3)
trans-3b	148.0-148.5	1.3584	1.8227	20.14 (20.22)	50.1 (50.3)
cis-4b	148.3-149.5	1.3602	1.8227	20.21 (20.22)	49.6 (50.3)
trans-4b	151.5-152.0	1.3615	1.8350	20.19 (20.22)	50.0 (50.3)
cis-5b	160.0-161.0	1.3569	1.8453	20.63 (20.62)	52.8 (53.1)
trans-5b	162.0-163.0	1.3607	1.8455	20.44 (20.62)	52.7 (53.1)
cis-6b	162.5-164.0	1.3561	1.8410	20.48 (20.62)	52.6 (53.1)
trans-6b	164.5-166.5	1.3577	1.8470	20.74 (20.62)	53.1 (53.1)
7b [e]	164.0-164.5	1.3523	1.8275	20.49 (20.62)	52.9 (53.1)
8b [f]	102.8-103.2	1.3293	1.7636	20.75 (20.63)	54.3 (54.4)

a) Except 1b, 2b, and 7b, all of these are new compounds. b) Boiling points are not corrected. c) Reported value; bp 114 °C, n_D^{25} 1.3620, see reference [1]. d) Calculated values in parentheses. e) Reported value; bp 171 °C, n_D^{25} 1.3494, see reference [1]. f) Cis/trans ratio determined by ^{19}F nmr = 1 : 0.6.

Fig. 1 ^{19}F nmr spectra of 1b, cis-2b, trans-2b, cis-3b, trans-3b, cis-4b, trans-4b, cis-5b, trans-5b, cis-6b, trans-6b, 7b, cis-8b, and trans-8b

Compound	Formula		Chemical shift^{a,b} (ppm)	J^{b} (Hz)
1b		a	73.4	a-c=c-a=17.4,
		b	104.5	a-e=e-a=4.5,
		c	125.3 J_{AB}	c-e=e-c=8.0,
		d	115.9	c-d=d-c=3.8,
		e	119.1 J_{AB}	b-d=d-b=11.7,
				b-e=e-b=4.2,
				d-e=228,
				b-c=244
cis-2b		a	76.4	a-c=c-a=17.5,
		b	110.9	a-b=b-a=2.5,
		c	118.5 J_{AB}	c-e=e-c=14.0,
		d	153.5	c-d=d-c=1.0,
		e	71.0	b-d=d-b=14.4,
				b-e=e-b=3.7,
				e-d=d-e=5.5,
				b-c=248
trans-2b		a	77.4	a-b=b-a=16.8,
		b	120.7	a-d=13.2,
		c	93.3 J_{AB}	a-c=c-a=1.8,
		d	163.1	c-e=e-c=14.5,
		e	71.3	c-d=1.7,
				b-d=8.1,
				b-e=e-b=2.1,
				e-d=5.7,
				b-c=254

a) ^{19}F chemical shifts in ppm relative to internal CCl_3F.

b) Only obvious chemical shifts and coupling constants are given.

Fig. 1 continued:

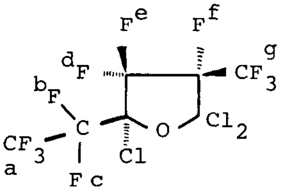
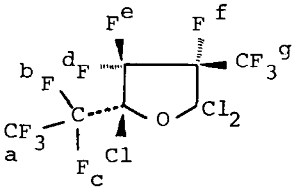
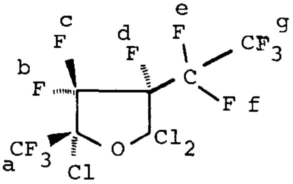
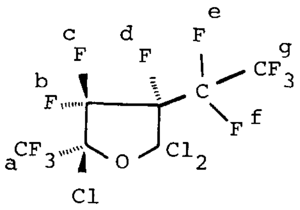
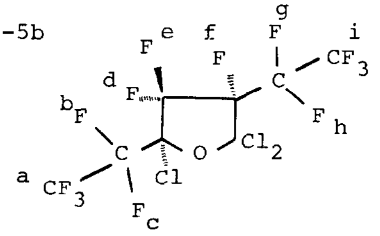
cis-3b		a	78.2		a-d=4.1,
		b			a-e=4.9,
		c			g-e=14.1,
		d	109.0	J_{AB}	g-d=3.6,
		e	117.0		g-f=f-g=5.2,
		f	152.6		f-d=14.7,
		g	70.9		d-e=254
trans-3b		a	77.8		g-e=15.0,
		b			g-d=2.3,
		c			g-f=5.7,
		d	118.5	J_{AB}	a-f=3.3,
		e	90.5		d-e=258
		f	162.0		
		g	71.5		
cis-4b		a	80.6		a-c=16.3,
		b	108.0	J_{AB}	a-b=12.2,
		c	117.1		d-g=g-d=17.9,
		d	154.1		d-b=14.7,
		e			b-c=254
		f			
		g	76.6		
trans-4b		a	81.0		a-b=15.8,
		b	117.9	J_{AB}	a-d=10.4,
		c	91.3		a-c=2.5,
		d	161.4		c-e=e-c=34.3,
		e	115.2	J_{AB}	c-f=f-c=19.4,
		f	120.2		e-b=3.6,
		g	77.5		e-d=3.6,
					f-d=4.8,
					b-c=255,
					e-f=300

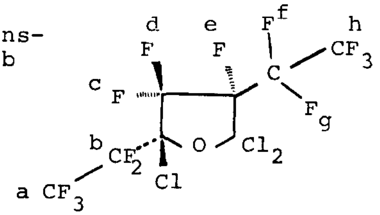
Fig. 1 continued:

cis-5b



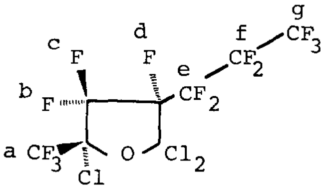
a	78.1		a-d=4.3,
b			a-e=4.3,
c			i-f=f-i=16.4,
d	106.9	J_{AB}	i-e=12.2,
e	116.7		f-d=16.2,
f	153.1		d-e=256
g			
h			
i	80.9		

trans-5b



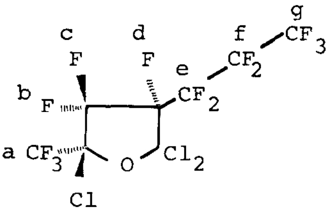
a	77.0		h-e=16.6,
b	119.9		h-d=9.8,
c	116.8	J_{AB}	a-c=3.0,
d	89.2		d-f=f-d=36.7,
e	161.7		d-g=g-d=19.8,
f	115.7	J_{AB}	c-d=254,
g	120.3		f-g=300
h	81.1		

cis-6b



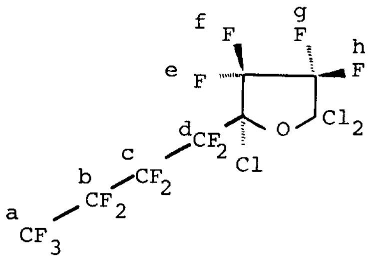
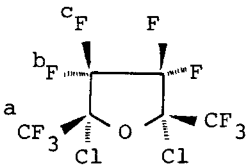
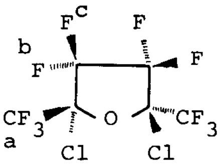
a	76.5		a-c=18.3,
b	107.8	J_{AB}	a-b=2.3,
c	117.4		g-e=11.5,
d	153.6		d-f=24.3,
e	113.5		d-b=15.3,
f	124.4		b-c=248
g	81.0		

trans-6b



a	77.9		a-b=18.3,
b	117.7	J_{AB}	a-d=12.7,
c	91.5		a-c=1.9,
d	161.7		g-e=11.5,
e	114.1		g-d=1.8,
f	125.1		b-c=254
g	81.1		

Fig. 1 continued:

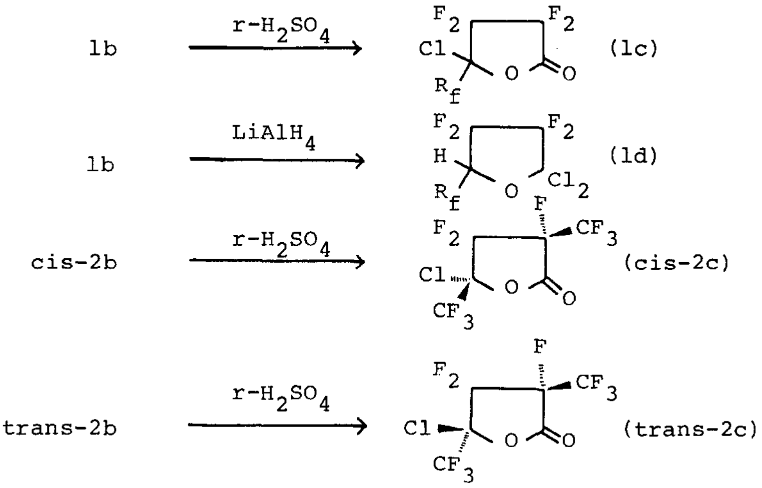
7b		a	80.7		a-c=10.2,
		b	125.9		a-d=2.4,
		c	117.5		f-d=27.4,
		d	114.4		f-c=9.0,
		e	108.2	J_{AB}	f-h=8.0,
		f	122.1		g-e=13.8,
		g	111.4	J_{AB}	e-f=242,
		h	120.0		g-h=226
cis-8b		a	77.8		b-c=230
		b	107.8	J_{AB}	
		c	128.2		
trans-8b		a	76.9		
		b,c	120.4		

In the case of trans-2b, trans-4b and trans-6b, through space coupling [J=10-13 Hz] was clearly observed between CF_3- and -F at the 2 and 4 positions of the oxolane ring that are cis to each other. This fact was the convincing evidence for the established trans structure of these compounds. Furthermore, the following few distinctions between cis and trans isomers were observed in the ^{19}F nmr spectra of B(2b-6b): (1) with respect to the -CF at the 4 position, the absorption peak appears at ϕ152.6-154.1 ppm for cis isomers, and at ϕ161.4-163.1 ppm for trans isomers, respectively. 2) with respect to the geminal $=CF_2$ at the 3 position, which show an AB pattern [J=248-254 Hz for cis, and J=254-258 Hz for trans isomers], the absorption peak of the fluorine, being trans to R_f groups at the 2 position, of the trans B(2b-6b), appears considerably down-field of those found for the cis B (2b-6b) [i.e. 89.2-93.3 ppm for trans, and 106.9-110.9 ppm for cis isomers, respectively].

Concerning the differences in the physical properties between cis and trans isomers of B(2b-6b), the cis isomers were found to have slightly lower boiling points, smaller refractive indexes, and lower densities than those of the trans isomers. These findings were very important with respect to the structural determination of the stereoisomers of the original A(2a-4a), as reported previously [4].

A parent peak was not found in the mass spectra of these compounds (B). Fragments corresponding to $[M-Cl]^+$ and $[M-R_f]^+$, where R_f represents the perfluoroalkyl groups at the 2 position, were always observed at intensities of 8-60% and 2-19% base, respectively.

Some reactions of 1b, cis-2b, and trans-2b are shown in Scheme 3. Hydrolytic reactions of 1b, cis-2b, and trans-2b with fuming H_2SO_4 afforded the corresponding perfluorolactones, i.e. 1c, cis-2c, and trans-2c, in yields of 99.2%, 92.0%, and 74.6%, respectively. Perfluorolactones so obtained were fuming clear liquids. Reaction of 1b with $LiAlH_4$ in ether gave volatile



Scheme 3

products, which were shown by GLC to consist of five minor and one major components. Among them, only 2-H-perfluoro-5,5-dichloro-2-methyloxolane (1d) was isolated by semi-preparative GLC (32.9%).

The ^{19}F nmr data of 1c, cis-2c, trans-2c and 1d are given in Fig.2 together with those of 1a, and other data (IR,Mass) are presented in the experimental section.

Fig. 2 ^{19}F nmr spectra of 1a, 1c, 1d, cis-2c, and trans-2c

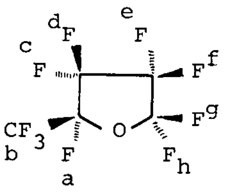
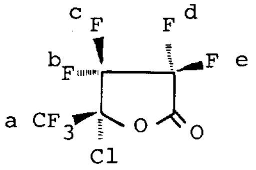
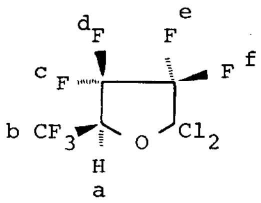
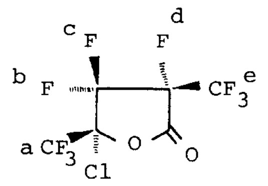
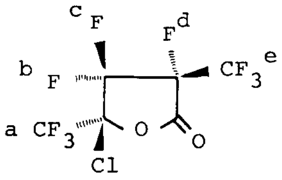
Compound	Formula		Chemical shift[a,b] (ppm)		J[b] (Hz)
1a		a	126.5		e-f=253
		b	80.8		
		c,d	128.9		
		e	126.9	J_{AB}	
		f	135.3		
		g,h	83.6		
1c		a	76.8		a-c=c-a=16.7,
		b	121.8	J_{AB}	a-b=2.8,
		c	127.8		a-e=2.8,
		d	116.5	J_{AB}	d-b=8.6,
		e	129.9		d-c=7.4,
					c-b=244,
					e-d=292
1d		a	9.3		a-b=b-a=5.4,
		b	74.0		b-d=13.9,
		c	108.2	J_{AB}	b-c=2.0,
		d	128.4		b-f=f-b=2.1,
		e	123.2	J_{AB}	c-d=250,
		f	119.7		e-f=226

Fig. 2 continued:

cis-2c		a b c d e	75.9 115.3] 125.3] J_{AB} 174.9 74.7	a-c=25.2, a-b=2.5, e-d=d-e=9.5, e-c=15.6, e-b=2.3, b-c=260, d-b=18.1
trans-2c		a b c d e	77.1 118.7] 108.9] J_{AB} 181.1 74.9	a-b=18.0, a-d=7.1, a-c=2.5, e-c=15.0, e-d=11.5, e-b=2.5, b-c=262

a) ^{19}F chemical shifts in ppm relative to internal CCl_3F, and a ^1H chemical shift in ppm down field from internal TMS.

b) Only obvious chemical shifts and coupling constants are given.

EXPERIMENTAL

Starting materials and apparatus

Except for perfluoro-2-n-butyloxolane (7a), the perfluorooxolanes used in this investigation were all made by the electrochemical fluorination of the proper starting materials. Perfluoro-2,4-dialkyloxolanes (2a-6a) were prepared by the fluorination of the α-alkyl-substituted carboxylic acids as reported previously [4]. Perfluoro-2-methyloxolane (1a) [6] and perfluoro-2,5-dimethyl oxolane (8a) were prepared by the fluorination of 2-methyloxolane [Tokyo Kasei Co.] and 2,5-dimethyloxolane [Aldrich Chemicals Co.] respectively. 8a was the new compound. All perfluorooxolanes thus obtained were purified by GLC. Perfluoro-2-n-butyloxolane (7a) was purchased from 3M Co. and used as it was.

The other reagents were available commercially and used as received.

Hoke bombs (capacity: 30, 75, and 150 ml) with stainless steel valves were used for the reactions of 1a-8a with $AlCl_3$, and a Pyrex vacuum line equipped with a Heise Bourdon tube gauge was used for handling the volatile compounds.

^{19}F nmr spectra were recorded on a Hitachi R-20B spectrometer at 56.4 MHz using $CFCl_3$ as an internal reference, while a ^1H nmr spectrum was recorded on a Hitachi R-22 spectrometer using TMS as an internal standard at 90 MHz. Infrared spectra were recorded on a Hitachi EPI-G3 spectrometer, and mass spectra on a Hitachi RMU-7 instrument at 70 eV.

Analytical work was carried out with Shimadzu GC-2C and GC-1C gas chromatographs using stainless steel columns (3 mm dia) packed with 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (6.4 m)(Col. A), 30% Kel F #3 on Chromosorb PAW (6.0 m)(Col. B), and 26% Kel F #90 on Chromosorb PAW (4.1 m)(Col. C). For semi-preparative work, a Shimadzu GC-1C gas chromatograph was used employing stainless steel columns (10 mm dia) packed with 30% Fluorolube HG 1200 on Chromosorb PAW (4.1 m)(Col. D).

Fluorination of 2,5-dimethyloxolane

The apparatus used and the fluorination procedures were the same as reported previously [4]. 2,5-Dimethyloxolane (30.0 g, 0.332 mo$l$) was charged into the cell which contained 1 l electrochemically purified anhydrous hydrogen fluoride, and the resulting solution was subjected to fluorination with an anodic current density of 3.5 A/dm^2, a cell voltage of 5.2-5.4 V, and a cell temp of 5-6 °C over a period of 398 min (214 Ahr) until the cell voltage rose rapidly (10 V.) The product collected in traps at -196 °C was roughly separated into two fractions using the traps of a low-temperature distillation unit. Fraction 1 (0.7 ml, 1.2 g) consisted mainly of CF_4 and small amounts of CHF_3 and C_2F_6. The Fraction 2 (40.0 ml, 68.9 g) was then subjected to GLC analysis (Col. A), and the following compounds were obtained: n-C_4F_{10} (3.5 g), perfluorooxolane (0.4 g), n-C_5F_{12} (0.6 g), 1a (0.6 g), perfluoro-2,5-dimethyloxolane (8a)(31.0 g, 29.5% Yield), cis-2a (3.2 g), trans-2a (2.5 g), perfluoro-2-methyloxane (20.2 g), perfluoro-3-methyloxane (0.9 g), and perfluorooxepane (1.0 g).

8a had bp 48.5-48.7 °C and d_4^{20}1.6765, which were different from those reported previously [4]. The compound assigned wrongly to 8a in the preceding paper has been revealed to be a previously unreported perfluoro-2-methyloxane. Detailed work on the synthesis of a series of the perfluoro(α-alkyl-substituted oxane)s will be reported later. 8a presented a very complex ^{19}F nmr spectrum. Hence, neither its detailed structure nor the constituent ratio of the cis and trans forms could be determined from it.

Perfluoro-2,5-dimethyloxolane (8a)(nc): IR (gas): 1352 (s), 1307 (w), 1210 (vs), 1232 (s), 1202 (w), 1162 (ms), 1107 (s), 949 (ms), 867 (m), 747 (w), 715 (m), 600 (w), 502 (w). Mass: 297 $[M-F]^+$(8.0), 219 $[M-CF_3]^+$(2.6), 150 $C_3F_6^+$(14.0), 147 $C_3F_5O^+$ (6.3), 131 $C_3F_5^+$(46.8), 119 $C_2F_5^+$(7.7), 100 $C_2F_4^+$(16.7), 97 C_2F_3O (19.6), 93 $C_3F_3^+$(5.1), 69 CF_3^+(100), 50 CF_2^+(4.7), 47 COF^+(6.9), 31 CF^+(14.8). Found: C, 22.50, F, 71.3%. Calculated for $C_6F_{12}O$ C, 22.79, F, 72.15%.

General procedure for the reaction of the perfluorocyclic ethers with $AlCl_3$

To illustrate the general procedure for this reaction, the respective reactions of 3a (as a typical example of the reaction of 1a-4a), 6a (as a typical example of the reaction of 5a-7a), and 8a with $AlCl_3$, will be described.

The reaction of 3a with $AlCl_3$

In a 30 m*l* Hoke bomb, 3a (3.25 g, 8.9 mmo*l*) was condensed onto granular $AlCl_3$ (3.5 g, 26.7 mmo*l*) and kept at 155-157 °C for 24 h. The 3a used was a mixture of cis and trans isomers, of which the constituent ratio was determined by GLC (Col. A) to be cis : trans = 45 : 55. The product was subjected to fractional condensation using traps at -40 °C, -98 °C, and -196 °C. The low boiling point compounds in the trap at -196 °C were primarily COC and small amounts of Cl_2 and HCl. In the second trap, mainly unchanged 3a and small amounts of CCl_4 were found. The trap at -40 °C contained a clear liquid. The compounds in the second and third traps were subsequently separated by GLC (Col. B, C). Thus, 3a (0.24 g), CCl_4 (0.25 g), cis-3b (0.89 g, 26.0% Yield), trans-3b (0.54 g, 15.8%) were obtained. Cis-perfluoro-2,5,5-trichloro-2-ethyl-4-methyloxolane (cis-3b)(nc): IR: 1345 (sh)(m), 1317 (s), 1290 (s), 1255-1237 (vs), 1213 (vs), 1188 (vs), 1150 (w), 1113 (m), 1090 (w), 1073 (m), 1048 (w), 1012 (s), 988 (s), 969 (m), 925-910 (m), 887 (m), 867 (m), 800 (m), 783 (m), 749 (m), 738 (ms) 729 (w), 717 (ms), 690 (w), 637 (m), 563 (w), 538 (w), 490 (w). Mass: 379 $[M-Cl^{35}]^+$(46.7), 295 $[M-C_2F_5]^+$(16.2), 247 $C_5F_8Cl^{35+}$(32.6), 163 $C_3F_4Cl^{35}O^+$(18.5), 147 $C_3F_5O^+$, $C_3F_4Cl^{35+}$(35.2), 135 $C_2F_4Cl^{35+}$ (34.4), 119 $C_2F_5{}^+$(30.1), 97 $C_2F_3O^+$(46.2), 85 CF_2Cl^{35+}(66.6), 69 $CF_3{}^+$(100), 63 $FOCl^{35+}$(51.2) (The chlorine isotope ratio was consistent with ion assignment, but the Cl^{37} ions have been omitted). Trans-perfluoro-2,5,5-trichloro-2-ethyl-4-methyloxolane (trans-3b) (nc): IR: 1338 (m)(sh), 1315 (s), 1281 (s), 1253 (s), 1255 (s)(sh), 1231 (vs), 1208 (s), 1193 (s), 1177 (s), 1153 (m), 1113 (w), 1090 (m), 1066 (s), 1016 (m), 1000 (vs), 910 (s), 886 (s), 863 (m), 787 (s), 728 (vs), 691 (w), 641 (m), 564 (w), 490 (w). Mass: 379 $[M-Cl^{35}]^+$(37.5), 295 $[M-C_2F_5]^+$(13.3), 247 $C_5F_8Cl^{35+}$(14.1), 197 $C_4F_6Cl^{35+}$(32.5), 163 $C_3F_4Cl^{35}O^+$(18.8), 147 $C_3F_5O^+$, $C_3F_4Cl^{35+}$ (33.6), 135 $C_2F_4Cl^{35+}$(30.5), 119 $C_2F_5{}^+$(30.3), 97 $C_2F_3O^+$(37.9), 85 CF_2Cl^{35+}(61.8), 69 $CF_3{}^+$(100), 63 $FOCl^{35+}$(48.3). Physical properties and analytical data, and ^{19}F nmr data of cis-3b and trans-3b are given in Table 3 and Fig. 1, respectively.

The reaction of 6a with $AlCl_3$

In a 30 m*l* Hoke bomb, 5.56 g (13.4 mmo*l*) of 6a and 3.6 g (27.1 mmo*l*) of $AlCl_3$ were held at 170 °C for 21 hr. The 6a used was a mixture of cis and trans isomers, of which the constituent ratio was determined by ^{19}F nmr to be cis/trans = 1 : 0.7.

Volatile products were collected by passing them through traps at -78 °C and -196 °C to a vacuum system. In the trap at -78 °C, unchanged 6a and CCl_4 were found.

The compounds which remained in the Hoke bomb were rinsed out several times with 10 m*l* of Daiflon S3 (1,1,2-trichloro-1,2,2 trifluoroethane). The solution was then removed from the green powder by filtration. After the major part of the solvent had be evaporated using a rotary evaporator, the liquid was analyzed by GLC (Col. C). Thus, the following compounds were obtained: cis-6b (1.47 g, 26.9% Yield), trans-6b (1.28 g, 23.4%), C_6Cl_6 (0.26 g). Cis-perfluoro-2,5,5-trichloro-2-methyl-4-n-propyloxolane (cis-6b)(nc): IR: 1347 (m), 1303 (s), 1275 (s)(sh), 1258 (s)(sh), 1240 (vs), 1206 (vs), 1167 (m), 1140 (s), 1085 (s), 1040 (m), 995 (m), 938 (s), 873 (s), 801 (s), 734 (s), 724 (s), 710 (m), 667-676 (w), 588 (w), 480 (w). Mass: 429 $[M-Cl^{35}]^+$(8.9) 395 $[M-CF_3]^+$(2.4), 197 $C_4F_6Cl^{35+}$(15.0), 147 $C_3F_5O^+$, $C_3F_4Cl^{35+}$(35. 85 CF_2Cl^{35+}(28.9), 69 CF_3^+(100), 63 $FOCl^{35+}$(38.8). Trans-perfluoro-2,5,5-trichloro-2-methyl-4-n-propyloxolane (trans-6b)(nc): IR: 1347 (s), 1297 (s), 1244-1259 (vs), 1221 (vs), 1206 (vs), 1172 (m), 1141 (vs), 1091 (s), 1073 (s), 1032-1038 (s), 1007 (m), 947 (s), 971 (m), 949 (w), 806 (m), 796 (m), 737 (vs), 731 (s), 717 (s), 670 (w), 593 (w), 481 (w). Mass: 429 $[M-Cl^{35}]^+$(9.0), 395 $[M-CF_3]^+$(2.7), 197 $C_4F_6Cl^{35+}$(17.6), 147 $C_3F_5O^+$,$C_3F_4Cl^{35+}$(38.8 85 CF_2Cl^{35+}(28.8), 69 CF_3^+(100), 63 $FOCl^{35+}$(41.1). Physical properties and analytical data, and ^{19}F nmr data of cis-6b and trans-6b are given in Table 3 and Fig. 1, respectively.

The reaction of 8a with $AlCl_3$

In a 30 m*l* Hoke bomb, 4.83 g (15.3 mmo*l*) of 8a and 4.1 g (30.5 mmo*l*) of $AlCl_3$ were held at 175 °C for 48 hr.

Purification was initially conducted by trap-to-trap distillation using traps at -98 °C and -196 °C. The compounds at -196 were Cl_2, HCl and $COCl_2$. The compounds retained at the -196 °C t were again subjected to trap-to-trap distillation using traps at -78 °C and -196 °C. The compounds at -196 °C were unchanged 8a which was slightly contaminated with $COCl_2$. The trap at -78 °C, retained the desired 8b together with small amounts of CCl_4 and C_6Cl_6. Gas chromatographic separation (Col. C) of the products at -78 °C yielded the following compounds: 8a (0.99 g), CCl_4

(0.03 g), 8b (0.74 g, 30.5% Yield), C_2Cl_6 (0.09 g). ^{19}F nmr studies of 8b revealed it to be a mixture of cis and trans forms, but they could not be separated by GLC. The cis:trans ratio determined by ^{19}F nmr was 1 : 0.6. Perfluoro-2,5-dichloro-2,5-dimethyloxolane (8b)(nc): IR: 1339 (m), 1303 (vs), 1267 (sh)(m), 1248 (vs), 1226 (vs), 1193 (s), 1166 (w), 1093 (s), 1072 (vs), 965 (m), 945 (s), 929 (m), 917 (m), 942 (s), 938 (s), 686 (w), 591 (w), 553 (w), 516 (w). Mass: 313 $[M-Cl^{35}]^+$(9.9), 279 $[M-CF_3]^+$(22.3), 166 $C_3F_6O^+$(12.8), 147 $C_3F_5O^+$,$C_3F_4Cl^{35+}$(53.1), 97 $C_2F_3O^+$(41.2), 85 CF_2Cl^{35+}(40.3), 63 $FOCl^{35+}$(11.3), 50 CF_2^+(8.5), 69 CF_3^+(100). Physical properties and analytical data, and ^{19}F nmr data of 8b are shown in Table 3 and Fig. 1, respectively.

The reaction conditions and yields used in the chlorination of the other perfluorooxolanes, including 3a, 6a and 8a, are summarized in Table 2.

Reaction of 1b with fuming H_2SO_4

In a Pyrex ampoule (1.3 X 15.0 cm), 3.2 g (10.1 mmol) of 1b and 2.6 g of fuming H_2SO_4 (20%) were kept at 143 °C for 17 hr.

The product consisted of two layers, the upper one being a transparent clear liquid, and the other a brown viscous liquid. The upper one, which fumes in the air, was carefully separated from the lower one using a separating funnel. Gas chromatographic separation (Col. C,D) yielded the following compounds: 1b (1.3 g), 1c (1.5 g, 99.2% Yield). Perfluoro-4-chloro-4-methyl-γ-butyrolactone (1c)(nc): bp 67.0-68.0 °C, n_D^{20}1.3212: IR (gas): 1877($\nu_{C=O}$) (s), 1359 (m), 1314 (w), 1284 (ms), 1249 (s), 1231 (vs), 1204 (s), 1163 (ms), 1111 (m), 1050 (vs), 1017 (s), 951 (ms), 872 (m), 729 (m), 631 (w), 560 (w), 352 (w), 474 (w). Mass: 197 $C_4F_6Cl^{35+}$(7.1), 166 $C_3F_5Cl^{35+}$(9.4), 147 $C_3F_4Cl^{35+}$,$C_3F_5O^+$(42.2), 131 $C_3F_5^+$(8.8), 100 $C_2F_4^+$(30.0), 79 $C_2F_3O^+$(31.9), 85 CF_2Cl^{35+}(18.2), 69 CF_3^+(100), 63 $COCl^{35+}$(14.9), 50 CF_2^+(19.7), 31 CF^+(35.7). Found: C, 22.60, F, 50.3%. Calculated for $C_5F_7ClO_2$: C, 23.03, F, 51.1%. ^{19}F nmr data of 1c are given in Fig. 2.

Reaction of 1b with $LiAlH_4$

In a 300 m*l* Pyrex bulb, 4.9 g (15.4 mmo*l*) of 1b was syringe onto 0.9 g of $LiAlH_4$ suspended in 10 m*l* of dry ether, and the reaction took place at 30-40 °C over a period of 2.5 hr.

Separation of the reaction mixture by trap-to-trap distillation resulted in the collection of clear liquids at -78 °C. Further purification by GLC (Col. A) afforded pure 1d (1.1 g, 32.9% Yield). Although small quantities of four kinds of compound other than 1d were obtained also, no detailed analytical work was conducted on these compounds. 2-*H*-perfluoro-5,5-dichloro-2-methyloxolane (1d)(nc): bp 91.5-92.0 °C, n_D^{20}1.3443, d_4^{20}1.6814: IR (gas) 1396 (s), 1353 (s), 1302 (s), 1302 (vs), 1261 (s), 1219 (vs), 1197 (vs), 1181 (sh)(m), 1124 (s), 1079 (vs), 1056 (sh)(m), 1008 (w), 918 (s), 868 (m), 848 (s), 791 (m), 768 (m), 712 (ms), 663 (m), 581 (w), 553 (w), 506 (w), 477 (w). Mass: 244 $C_5F_7OCl^{35+}$ (26.6), 131 $C_3F_5^+$(10.2), 112 $C_3F_4^+$(100), 85 CF_2Cl^{35+}(27.6), 63 $COCl^{35+}$(42.0), 51 CF_2H^+(11.4), 50 CF_2^+(8.2), 31 CF^+(15.2). Found: C, 21.20, F, 46.7%. Calculated for $C_5F_7HCl_2O$: C, 21.35, F, 47.3%. ^{19}F nmr data of 1d are given in Fig. 2.

Reaction of cis-2b with fuming H_2SO_4

In a Pyrex ampoule (1.3 X 14.0 cm), 3.2 g (8.8 mmo*l*) of cis-2b, 9.9 g of fuming H_2SO_4 (20%) and a trace of yellow HgO were held at 145 °C for 24 hr. The reaction products consisted of two layers. The transparent upper layer was separated from the lower one in a manner similar to that described for the reaction of 1b.

The liquid thus obtained (2.5 g, 1.6 m*l*) needed no further purification by GLC, and was assigned as pure cis-2c based on ^{19}F nmr (Fig. 2), mass, and infrared analysis, and elemental analyses (C and F). The yield of cis-2c was 92.0%. Cis-perfluoro-4-chloro-2,4-dime γ-butyrolactone (cis-2c)(nc): bp 84.0-84.5 °C, n_D^{20}1.3172. IR (gas): 1897($\nu_{C=O}$)(s), 1324 (s), 1289 (vs), 1262 (vs), 1244 (m), 1226 (vs), 1157 (ms), 1136 (m), 1080 (vs), 1026 (w), 984 (s), 951 (s), 840 (ms), 746 (w), 732 (w), 707 (ms), 652 (w), 504 (w). Mass: 291 $[M-F]^+$(0.6), 275 $[M-Cl^{35}]^+$(3.9), 247 $C_5F_8Cl^{35+}$(2.2), 231 $C_5F_9^+$(1.8), 197 $C_4F_6Cl^{35+}$(14.1), 159 $C_4F_5O^+$(8.3), 150 $C_3F_6^+$(17.3), 147 $C_3F_5O^+$,$C_3F_4Cl^{35+}$(13.4), 131 $C_3F_5^+$(11.0), 100 $C_2F_4^+$(21.3), 97 $C_2F_3O^+$(17.4), 85 CF_2Cl^{35+}(10.8), 69 CF_3^+(100), 63 $COCl^{35+}$(14.9), 50 CF_2^+(6.7), 31 CF^+(22.4). Found: C, 23.10, F, 54.5%. Calculated for $C_6F_9ClO_2$: C, 23.19, F, 55.1%. ^{19}F nmr data of cis-2c are given in Fig. 2.

Reaction of trans-2b with fuming H_2SO_4

Analogously to the reaction described above, a reaction mixture of 3.0 g (8.2 mmol) of trans-2b, 10.6 g of fuming H_2SO_4 (20%), and small amounts of yellow HgO were kept at 145 °C for 24 hr. The clear liquid which was separated from the brown liquid layer was found to be pure trans-2c (1.9 g, 74.6% Yield). Trans-perfluoro-4-chloro-2,4-dimethyl-γ-butyrolactone (trans-2c) (nc): bp 86.0-86.5 °C, n_D^{20}1.3202. IR (gas): 1869 ($\nu_{C=O}$)(s), 1289-1318 (s), 1259 (vs), 1228 (vs), 1156 (s), 1138 (ms), 1080 (vs), 1026 (w), 987 (s), 953 (s), 842 (ms), 748 (m), 733 (m), 708 (ms), 651 (w), 503 (w). Mass: 291 $[M-F]^+$(0.7), 275 $[M-Cl^{35}]^+$(4.5), 247 $C_5F_8Cl^{35+}$(2.0), 231 $C_5F_9^+$(2.1), 197 $C_4F_6Cl^{35+}$(19.8), 159 $C_4F_5O^+$(5.2), 150 $C_3F_6^+$(21.0), 147 $C_3F_5O^+$,$C_3F_4Cl^+$(17.8), 131 $C_3F_5^+$(9.2), 100 $C_2F_4^+$(22.0), 97 $C_2F_3O^+$(18.8), 85 CF_2Cl^{35+}(15.5), 69 CF_3^+(100), 63 $COCl^{35+}$(24.6), 50 CF_2^+(6.2), 31 CF^+(20.3). Found: C, 23.15, F, 55.0%. Calculated for $C_6F_9ClO_2$: C, 23.19, F, 55.1%. ^{19}F nmr data of trans-2c are given in Fig. 2.

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