The Electrochemical Fluorination of Aliphatic Primary Monohydric Alcohols and Aldehydes[1]

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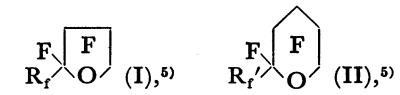
The perfluorocyclic ethers as well as the perfluoroalkanoyl fluorides were obtained by the electrochemical fluorination of primary monohydric alcohols and aldehydes containing 4—8 carbon atoms. The five-membered rather than the six-membered perfluorocyclic ethers were formed as the cyclic products. The over-all yields of the perfluorocyclic ethers and the perfluoroalkanoyl fluorides from the alcohols were in the range of 10—20%, and 3—12% respectively. Those from the aldehydes were poor because of the formation of a considerable amount of tarry by-products. The physical properties of the perfluorocyclic ethers obtained are also described.

The electrochemical fluorination of diols, which resulted primarily in the formation of the six-membered perfluorocyclic ethers, was studied previously.[2]

Commonly, perfluorocyclic ethers (I and II) are known to be formed as the cyclization products in the electrochemical fluorination of straight chain carboxylic acids and their acid halides,[3] or of cyclic ethers directly.[4] The corresponding perfluoroalkanoyl fluorides (III) are also formed in the former case

$$CH_3(CH_2)_nC(O)X \xrightarrow[\text{fluorination}]{\text{Electrochemical}} \left(\begin{matrix} n\geqq 2 \\ X=OH, \text{ halogen}\end{matrix}\right)$$



$$\left(R_f=C_{n-2}F_{2n-3},\ n\geqq 2\right) \quad \text{(I)},^{5}$$

$$\left(R_f'=C_{n-3}F_{2n-5},\ n\geqq 3\right) \quad \text{(II)},^{5}$$

$$CH_3(CF_2)_nC(O)F \quad \text{(III)}$$

To investigate the behavior of alcohols upon electrochemical fluorination in more detail, we examined next the fluorination of several monohydric alcohols. It was found that primary monohydric alcohols also give the perfluorocyclic ethers as well as the perfluoroalkanoyl fluorides in considerable yields, which provides an additional useful route for the preparation of perfluorocyclic ethers.

This paper will deal with the electrochemical fluorination of alcohols and aldehydes having 4—8 carbon atoms, and with the characterization of the products and their related compounds.

Results and Discussion

The reaction conditions and the results of the fluorination of alcohols and aldehydes are shown in Tables 1 and 2 respectively.

The alcohols were dissolved in anhydrous hydrogen fluoride (AHF) to give a colorless electroconductive solution, while the aldehydes (butanal, pentanal, hexanal, heptanal, and octanal) gave a colored solution. The butyric aldehyde–AHF solution had a yellowish tint, and the others had a brownish one.

These solutions containing oxonium ion species were electrolysed smoothly and afforded perfluoroalkanes, perfluorocyclic ethers, and perfluoroalkanoyl fluorides as exhaustive fluorination products. On fluorination of most of the alcohols, only a very small amount of the perfluoroalkanes having the same number of carbon atoms as the starting materials was produced. However, there was a tendency for the formation of an increased amount of the perfluoroalkanes which comprise the same carbon skelton as the sample on fluorination of branched alcohols with an alkyl group on the β carbons, such as 2-ethyl-1-butanol and 2-methyl-1-pentanol.[6] The perfluoroalkanes having one fewer carbon atom than the starting materials and acyl fluorides were invariably formed as the principal cleaved products.

Fluorination of the Alcohols Having Linear Alkyl Groups (Runs 1—7 in Table 1). These alcohols afforded the perfluorocyclic ethers in fair yields. While the yields of the perfluoroalkanoyl fluorides decreased steadily with increase in the length of the carbon chain of the alcohols, the highest yield (21.7%) of the perfluorocyclic ethers was obtained in the case of 1-pentanol (Run 2). This may be due to the availability of the largest number of the C–H bonds on the δ and ε carbons of the alcohol, to create a carbon radical, and also due to the easier mobility of the alkyl group towards the carbonyl oxygen, which occurs intramolecularly, to form a 5-membered or 6-membered ring.

The perfluorocyclic ethers thus obtained consisted almost of the 5-membered and its isomeric 6-membered ring compounds. When the perfluorotetrahydrofurans contain side chains, they were on the 2-position of the ring. However, in the case of the perfluorotetrahydropyrans, ^{19}F NMR revealed that the side chain attached to the 3- or 4-positions of the pyran ring but not to the 2-position as has hitherto been reported.[3a]

The yields of the perfluorotetrahydrofuran from the alcohols with unsaturated bonds at γ carbon (Run 6 and 7) increased slightly, compared with the results in Run 1.

Fluorination of the Alcohols Having Side Chains (Runs 8—12 in Table 1). In Run 8, the perfluoro-2-methyltetrahydrofuran rather than the perfluoro-3-methyltetrahydrofuran was obtained as the major cyclization product. In Run 10, the yield of perfluoro-3,3-dimethyltetrahydrofuran, the expected cyclization product from fluorination of 3,3-dimethyl-1-butanol alcohol, was very poor (<1%), in spite of a sufficient number of available C–H bonds (9) of the starting material for the formation of the 5-membered ring. Instead, perfluoro-2,3-dimethyltetrahydrofuran, perfluoro-3-ethyltetrahydrofuran, perfluoro-2,5-dimethyl-

Table 1. Summary of the fluorination of monohydric alcohols

Anodic current density, 3.5 A/dm²; cell temp, 5—6 °C; volt, 5—10 V; sample, 0.20 mol

Run	Sample	Electricity passed (A h)	Fluorinated compounds obtained (g)	Ag salt of the perfluorocarboxylic acids obtained (g)	Perfluorocyclic ethers and perfluoroalkanoyl fluorides (Yield, mol %)
1	1-Butanol	119	16.3	11.8(11.8)[a]	$\overline{CF_2CF_2CF_2CF_2O}$ (IX) (11.7)
2	1-Pentanol	131	22.5	12.0(11.6)	$\overline{CF(CF_3)CF_2CF_2CF_2O}$ (X) (18.2), $\overline{CF_2CF_2CF_2CF_2CF_2O}$ (XI) (3.5)
3	1-Hexanol	143	25.3	6.9 (6.5)	$\overline{CF(C_2F_5)CF_2CF_2CF_2O}$ (XII) (8.6), $\overline{CF(CF_3)CF_2CF_2CF(CF_3)O}$ (XIII) (2.8), $\overline{CF_2CF(CF_3)CF_2CF_2CF_2O}$ + $\overline{CF_2CF_2CF(CF_3)CF_2CF_2O}$ (XIV)[b] (1.4), $\overline{CF_2CF_2CF_2CF_2CF_2CF_2O}$ (XV) (trace)
4	1-Heptanol[c]	151	34.5[d]	3.2 (2.3)	$\overline{CF(C_3F_7)CF_2CF_2CF_2O}$ (XVI) (10.3), $\overline{CF_2CF(C_2F_5)CF_2CF_2CF_2O}$ + $\overline{CF_2CF_2CF(C_2F_5)CF_2CF_2O}$ (XVII)[e] (0.9)
5	1-Octanol[c]	161	28.1[f]	3.2 (1.6)	$\overline{CF(C_4F_9)CF_2CF_2CF_2O}$ (XVIII) (10.3)
6	3-Buten-1-ol[g]	60	8.5	4.8 (4.8)	IX (14.1)
7	3-Butyn-1-ol[h]	59	9.7	5.3 (5.3)	IX (14.2)
8	3-Methyl-1-butanol	134	22.4	7.3 (4.8)	$\overline{CF_2CF(CF_3)CF_2CF_2O}$ (3.6), X (8.6), XI (2.6), $C_2H_5CF(CF_3)C(O)F$ (3.2)
9	3-Methyl-1-pentanol	163	28.8	3.8 (3.7)	$\overline{CF(CF_3)CF(CF_3)CF_2CF_2O}$ (XIX) (8.4), $\overline{CF_2CF(C_2F_5)CF_2CF_2O}$ (XX) (8.5), XIII (2.2), $\overline{CF_2CF_2CF(CF_3)CF_2CF_2O}$ (XXI)[i] (2.6), XV (0.5)
10	3,3-Dimethyl-1-butanol	173	30.8	3.2 (3.0)	$\overline{CF_2C(CF_3)_2CF_2CF_2O}$ (0.9), XIX (9.9), XX (6.1), XIII (3.0), XXI (2.3), XV (trace)
11	2-Ethyl-1-butanol	163	28.3	—	XX (6.4), $(C_2F_5)_2CFC(O)F$ (5.5)

a) Ag salt of the perfluoro carboxylic acid obtained, with the same carbon numbers as the samples (calculated by analysing the methyl ester derivatives of the corresponding perfluoro carboxylic acids). b) Bp 59.5—60.0 °C. Found: F, 72.2%. Calcd: F, 72.8%. c) Sample fed, 0.19 mol. d) 7.1 g were obtained as cell drainings. e) Bp 84.5—85.0 °C. Found: F, 72.7%. Calcd: F, 73.0%. f) 10.9 g were obtained as cell drainings. g) Sample fed, 0.11 mol. h) Sample fed, 0.13 mol. i) Contaminated with a considerable amount of perfluoro-3-methyltetrahydropyran.

Table 2. Summary of the fluorination of aldehydes

Anodic current density, 3.5 A/dm²; cell temp, 5—6 °C; volt, 5—10 V; sample, 0.20 mol

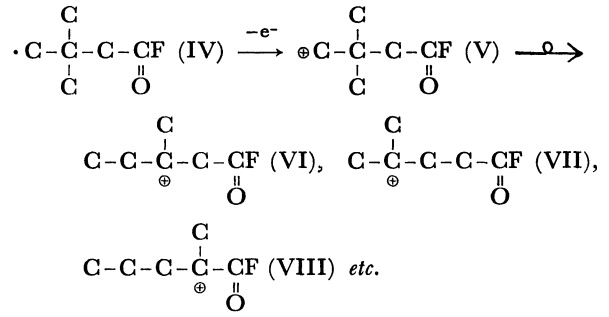
Run	Sample	Electricity passed (A h)	Fluorinated compounds obtained (g)	Ag salt of the perfluoro carboxylic acids obtained (g)	Perfluoro cyclic ethers (Yield, mol %)
1	Butanal	85	11.9	7.2(7.2)[b]	IX (5.9)
2	Pentanal	113	12.3	4.2(2.8)	X (3.9), XI (1.3)
3	Hexanal	136	12.8	2.1(1.4)	XII (3.0), XIII (1.3), XIV (0.6)
4	Heptanal[a]	137	19.1	2.8(1.4)	XVI (3.9), XVII (0.3)
5	Octanal[a]	143	9.8	1.5(—)	XVIII (trace)

a) Sample fed, 0.19 mol. b) Ag salt of the perfluoro carboxylic acid obtained, with the same carbon numbers as the samples.

tetrahydrofuran, and perfluoro-4-methyltetrahydropyran were obtained as cyclic products. On the other hand, the fluorination of 3-methyl-1-pentanol (Run 9) afforded almost the same kinds of products as in the case of 3,3-dimethyl-1-butanol (Run 10). Perfluorotetrahydrofurans with perfluoroalkyl groups attached to the expected position of the ring could be obtained satisfactorily in other Runs. Thus, the rearrangement which involves the 1,2-shift of the methyl group of the starting material (3,3-dimethyl-1-butanol) in competition with the cyclization is very likely to take place through the fluorination.

Although an unequivocal explanation has not yet been made of the mechanisms of the electrochemical fluorination,[7] a free radical type reaction is generally accepted. However, so far as the isomerization in the course of the fluorination is concerned, the rearrangement of alkyl groups *via* carbonium ion intermediate is more attractive rather than the free radical type rearrangement,[8] since the alkyl radicals do not generally rearrange.[9] The Hofer-Moest reaction, an example of Kolbe electrolysis, is known to proceed not only in the radical process but also mainly through the carbonium ion process.[9] Similarly, the fluorination by the electrochemical process may be interpreted in terms both of the free radical and the ionic reaction.

Thus, the acyl fluoride formed by the elimination of hydrogen fluoride from unstable α,α-difluoro alcohols (postulated initial fluorination product from alcohols) may be subjected to hydrogen abstraction by fluorine to give a free radical (IV). Then the expected 3,3-dimethyltetrahydrofuran may be created by the intramolecular cyclization. However, the major part of IV may rearrange competitively into other acyl fluorides *via* V, which resulted from further anodic oxidation of the radical of IV. The methyl group on the γ carbon of the intermediate compound (V) migrates favorably in such a way as to produce more stable tertiary carbonium ions. With a highly branched starting material, more opportunities will be given for such an rearrangement than for the cyclization.



The carbonium ion of acyl fluoride (VI) can proceed to the corresponding perfluoroalkanoyl fluoride, but generally it will lead to the cyclic ethers by the intramolecular attack of one of the radicals formed on the three different carbons (denoted by a, b, and c) to the carbonyl oxygen atom. The cyclization which can proceed to the formation of three isomeric perfluorocyclic ethers is formulated as follows:

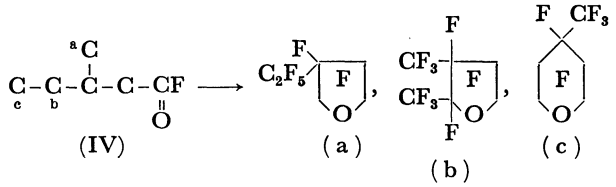


Table 3. Properties of perfluorocyclic ethers and perfluoroalkanoyl fluorides

Compound	Bp (°C)	d_4^{20}	Elemental analysis C (%)	Elemental analysis F (%)
$CF_2CF(CF_3)CF_2CF_2O$	28.5—29.0			71.5(71.3)[a]
$CF(C_2F_5)CF_2CF_2CF_2O$[b]	54.0—55.5	1.6944		72.1(72.2)
$CF(C_3F_7)CF_2CF_2CF_2O$[c]	75.2—75.5	1.7475	22.56(22.95)[a]	72.8(72.7)
$CF(C_4F_9)CF_2CF_2CF_2O$[d]	99.0—99.5	1.7847	22.96(23.08)	73.7(73.1)
$CF(CF_3)CF_2CF_2CF(CF_3)O$	53.5—54.0	1.7321		71.6(72.2)
$CF(CF_3)CF(CF_3)CF_2CF_2O$[e]	52.9—53.3	1.7063		72.3(72.2)
$CF_2CF(C_2F_5)CF_2CF_2O$	55.2—55.8	1.7200		72.3(72.2)
$CF_2C(CF_3)_2CF_2CF_2O$	57.2—57.7	1.7618	22.37(22.79)	72.2(72.2)
$CF_2CF(CF_3)CF_2CF_2CF_2O$[f]	58.2—59.0	1.7662	22.73(22.79)	72.5(72.2)
$C_2F_5CF(CF_3)C(O)F$[g]	29.5—31.5			71.0(71.3)
$(C_2F_5)_2CFC(O)F$	54.9—55.2	1.6721	22.98(22.79)	72.2(72.2)

a) Calculated values are given in parentheses. b) Reported bp 54—55 °C, d_4^{20} 1.6864, n_D^{20} 1.2640, see Ref. 4b. c) Reported bp 78—79 °C, d_4^{20} 1.7285, n_D^{20} 1.2724, Ref 4b. d) n_D^{20} 1.2795, reported bp 100—102 °C/741 Torr d_4^{20} 1.7660, n_D^{20} 1.2775, Ref 4b. see also the Technical Bulletin "Inert Fluorochemical Liquids FC-75," Minnesota Mining and Manufacturing Co., where extensive physical data are given. e) Mixed with small portions of perfluoro(2-ethyltetrahydrofuran). Estimated purity 80%. f) Isolated and purified from the products which were obtained by the fluorination of 2-methylamyl alcohol, see Ref. 6. g) Reported bp 23—26 °C, F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

The perfluoro-3-methyltetrahydropyran, which is mixed with perfluoro-4-methyltetrahydropyran as an inseparable contaminant, is considered to be produced by the cyclization of VII and VIII. The properties of these perfluorocyclic ethers are shown in Table 3.

It is noteworthy that perfluoro-2-methylbutyryl fluoride $C_2F_5CF(CF_3)C(O)F$, and perfluoro-2-ethylbutyryl fluoride $(C_2F_5)_2CFC(O)F$, obtained in Runs 8 and 11 respectively, were collected safely in cold traps, after passing through a series of washing bottles containing 5% aqueous potassium hydroxide solution.

Some spectral data (^{19}F NMR and IR) of perfluoro-2-methylbutyryl fluoride and perfluoro-2-ethylbutyryl fluoride are shown in Table 4.

Table 4. ^{19}F NMR[a] and IR data of the perfluoro-2-methylbutyryl fluoride and perfluoro-2-ethylbutyryl fluoride

$CF_3-\overset{F'}{\underset{F''}{C}}-\overset{}{CF}-CF_3$	$CF_3-\overset{F'}{\underset{F''}{C}}-\overset{}{CF}-\overset{F'}{\underset{F''}{C}}-CF_3$
$\overset{}{\underset{F}{C=O}}$	$\overset{}{\underset{F}{C=O}}$
122.9 180.3	120.9 179.5
83.2 72.7	81.3
118.5 −32.5	118.0 −33.7
$J_{F'F''}=293$	$J_{F'F''}=298$
ν (C=O); 1890 cm^{-1} (vs), 1878 cm^{-1} (ms, sh)	ν (C=O); 1885 cm^{-1} (vs)

a) Chemical shifts and J values are given in ϕ (internal CCl_3F reference) and Hz respectively.

Generally, perfluoroalkanoyl fluorides of the type $R_fC(O)F$ (R_f=linear perfluoroalkyl group) hydrolyze very easily into the corresponding perfluoro carboxylic acids. The anomalies in hydrolytic stability of these perfluoroalkanoyl fluorides with the side chain on the α carbon may be ascribed to the spatial shielding of the carbonyl carbon by two perfluoroalkyl groups.

Fluorination of the Aldehydes. The fluorination of aldehydes gave a formation and distribution of the products similar to that obtained with the alcohols (Runs 1—5 in Table 1). However, the yields both of the perfluorocyclic ethers and the perfluoroalkanoyl fluorides were lower, and the formation of a considerable amount of tarry material in the cell was observed in each run. The polymerization of aldehydes in AHF, which gives a colored liquid of low-molecular weight, has been reported briefly in the literature.[11]

Experimental

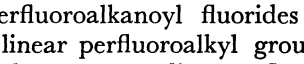
Reagents and Apparatus. All reagents except 3,3-dimethyl-1-butanol, which was prepared by the reaction of 3,3-dimethylbutyryl chloride with lithium aluminium hydride in ether, were available from Tokyo Kasei Co.. Anhydrous hydrogen fluoride (AHF) was more than 99.5% pure. The electrolytic cell used was the same as that described in a previous paper.[12] A standard Pyrex vacuum line was used in the reaction of perfluoro-2,3-dimethyltetrahydrofuran with aluminum chloride for handling the volatile liquids and gaseous materials.

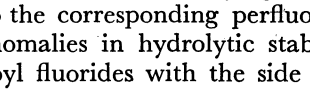
The IR spectrum measurements were made on a Hitachi EPI-G3 spectrometer, using a 6 cm gas cell with KBr windows. The ^{19}F NMR spectra were obtained on a Hitachi Model R-20B high resolution spectrometer operating at 56.46 MHz.

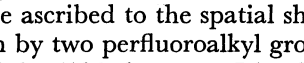
General Procedures for the Electrochemical Fluorination of Alcohols and Aldehydes. A typical example is the case of the fluorination of 3,3-dimethyl-1-butanol (Run 10 in Table 1). A 20.2 g portion of 3,3-dimethyl-1-butanol was dissolved in 1 l AHF in the cell. Then the electrolysis was carried out with an anodic current density of 3.5 A/dm^2, a cell temperature of 5—6 °C, and a cell voltage of 5 V, which rose gradually as the fluorination proceeded. The operation was continued until the voltage reached 10 V. Thus 173 Ahr of electrolysis was conducted.

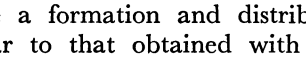
The effluent gases from the cell were passed over NaF pellets, and then bubbled through two consecutive polyethylene bottles containing water (for collection of the perfluorocarboxylic acids resulting from the hydrolysis of the corresponding perfluoroalkanoyl fluorides). The gaseous products which did not react with water were further guided into an alkaline solution of potassium sulfite, and finally collected in traps immersed in liquid nitrogen.

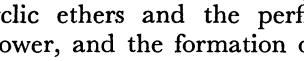
(A) Analysis of the Perfluorocyclic Ethers: The products (30.8 g) condensed in the cold traps were initially subjected to low-temperature distillation, giving two fractions; fraction 1 (bp<0 °C, 3.3 g) and fraction 2 (25.7 g, 15.7 ml). The fraction 1 consisted mainly of CF_4, C_2F_6, and C_3F_8. The fraction 2 was carefully redistilled to collect the volatile compounds. Perfluoropentanes (a mixture of *n*- and isopentane, *n*-C_5F_{12}: *iso*-C_5F_{12}=57: 43) were obtained at about 25 °C as the main low boiling component. The distillation residue (16.7 g, 10.3 ml) was then further subjected to gas chromatographic analysis (compositions were calculated on the basis of chromatographic peak areas, assuming equal weight sensitivities for all components). Thus the following perfluorocyclic ethers were detected:


0.6 g,


6.3 g,


3.8 g,


1.9 g,


1.4 g.

The perfluoro-4-methyltetrahydropyran obtained was found to be mixed with almost an equal quantity of the perfluoro-3-methyltetrahydropyran from the ^{19}F NMR spectrum; 4-CF_3-*cyclo*-C_6F_9O: 3-CF_3-*cyclo*-C_6F_9O=50: 50. In addition to these perfluorocyclic ethers, the formation of perfluorohexamethylene oxide was also observed.[10] With the exception of perfluoro-2,3-dimethyltetrahydrofuran, the isolation and purification of these isomeric perfluorocyclic ethers were accomplished by means of repeated gas chromatography. The preparative-scale columns packed with Silicone QF-1 30% on Chromosorb PAW, diester of hexamethylene glycol with perfluorooctanoic acid 20% on Chromosorb PAW, and 1,6-bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyloxy)-hexane 30% on Chromosorb PAW were employed. These compounds were characterized by ^{19}F NMR, IR, and mass as well as elemental analyses. The perfluoro-2,3-dimethyltetrahydro furan obtained was found to be contaminated with a small amount of perfluoro-2-ethyltetrahydrofuran, from its spectrometric data (IR and ^{19}F NMR). However, it was not possible to separate them by the preparative gas chromatography. Therefore, the characterization of these compounds was subsequently achieved by converting them into the corresponding perfluoro-2,5,5-trichlorotetrahydrofuran

derivatives followed by the gas chromatographic separation according to a method described in the literature.[13]

Reaction of Perfluoro-2,3-dimethyltetrahydrofuran with $AlCl_3$: In a 30 ml stainless steel bomb, 1.0 g of anhydrous granular $AlCl_3$ and 1.57 g of perfluoro-2,3-dimethyltetrahydrofuran, which contained perfluoro-2-ethyltetrahydrofuran, were kept at 145 °C overnight. Purification was initially conducted by trap-to-trap distillation, using traps immersed in cold baths kept at −78 °C and −196 °C respectively. The gas chromatographic separation of the products which were retained in the −78 °C trap yielded two major fractions along with some unreacted starting material, carbon tetrachloride, and hexachloroethane. These fractions were assigned to be perfluoro-2,5,5-trichloro-2,3-dimethyltetrahydrofuran and perfluoro-2,5,5-trichloro-2-ethyltetrahydrofuran on the basis of their spectroscopic data and elemental analyses.

Perfluoro-2,5,5-trichloro-2,3-dimethyltetrahydrofuran: Yield: 0.82 g (52%), bp 132.5—133.5 °C, n_D^{20} 1.3627, d_4^{20} 1.7977. Found: C, 19.50; F, 46.8%. Calcd: C, 19.70; F, 46.8%.

Perfluoro-2,5,5-trichloro-2-ethyltetrahydrofuran: Yield: 0.21 g (13%), bp 131.0—131.5 °C (lit,: 136 °C),[13] n_D^{20} 1.3605 (lit,: n_D^{25} 1.3566),[13] d_4^{20} 1.7817. Found: C, 19.62; F, 46.7%. Calcd: C, 19.70; F, 46.8%.

(B) Analysis of the Perfluorocarboxylic Acids: The analysis of the perfluoroalkanoyl fluorides produced was performed through their methyl esters. The aqueous solution of the perfluoro carboxylic acids in the polyethylene bottles was neutralized by adding anhydrous Na_2CO_3, and the solution was evaporated to dryness, giving a white solid. It was extracted with alcohols and the extract was evaporated to dryness to give a pure sodium salt. Then the salt was acidified with 10% aqueous H_2SO_4, and free acid was extracted with ether. The ethereal solution of perfluoro carboxylic acid was treated with Ag_2O and filtered, and then the filtrate was evaporated to afford a dry silver salt. In a 50 ml three-necked flask fitted with a reflux condenser, a dropping funnel, and a thermometer, 3.3 g of the fine powdered silver salt and 20 ml of 1,1,2-trichloro-1,2,2-trifluoroethane were placed and heated to 70 °C, with stirring by a magnetic stirrer. Methyl iodide (3 g) was added to the mixture from the dropping funnel over a period of 30 min. The resulting mixture was kept with stirring for an additional 3 h. After removal of silver iodide by filtration, the solvent and unreacted methyl iodide were evaporated. Then, the preparative gas chromatography (column: Kel F #90 26% on Chromosorb PAW; carrier gas: He) of the residue evaporated gave 1.2 g of the mixtures of methyl esters of perfluoro carboxylic acid consisting of $C_3F_7C(O)OCH_3$ (3, peak area %), $C_4F_9C(O)OCH_3$ (2), and $C_5F_{11}C(O)OCH_3$ (95). A few shoulders, which suggested the presence of isomers, appeared on the peak of the gas chromatogram which corresponded to the methyl ester of perfluorohexanoic acid. No further analysis of these isomers was conducted.

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3) a) E. A. Kauck and J. H. Simons, U. S., 2644823 (1953); b) Saline Ludwigsshalle A. G., Germ. 1069639 (1959); c) Minnesota Mining and Manufacturing Co., Brit., 1007288 (1965); d) W. Blöchl, Fr., 1436269 (1966).

4) a) Minnesota Mining and Manufacturing Co., U. S., 2594272 (1952); Brit., 672720 (1952); b) I. P. Kolenko, N. A. Ryabinin, and B. N. Lundin, *Tr. Inst. Kim., Akad. Nauk SSSR, Ural Filial*, **1968**, 59.

5) The symbol(F) indicates perfluorinated alicyclic ring.

6) The fluorination of this compound gave the mixture of *cis*- and *trans*-perfluoro-2,4-dimethyltetrahydrofuran as the main cyclization product; this could be separated into almost pure *cis*- and *trans*-forms by gas chromatography. Detailed work will be published elsewhere by T. Abe.

7) N. Watanabe and M. Haruta, "Fussokagaku to Kogyo," Vol. II ed. by N. Watanabe, Kagakukogyosha, Tokyo (1973), p. 122.

8) J. Burdon and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. 1, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworth Scientific Publications, London (1960), p. 144.

9) C. Walling, "Molecular Rearrangement," Vol. I, ed. by P. D. Mayo, Interscience Publishers, New York (1963), p. 416.

10) To be published.

11) S. Murahashi and S. Sakakibara, *Yuki Gosei Kagaku*, **25**, 109 (1967).

12) T. Abe, S. Nagase, and H. Baba, *Bull. Chem. Soc. Jpn.*, **46**, 3845 (1973).

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