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SYNTHESIS OF PERFLUOROBICYCLIC ETHERS [1]. THE ELECTROCHEMICAL FLUORINATION OF CYCLOALKYL-SUBSTITUTED CARBOXYLIC ACIDS*

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SUMMARY

A new synthetic method for making perfluorobicyclic and perfluoromonospiro ethers by fluorinating the cycloalkyl-substituted carboxylic acid electrochemically is presented. Novel perfluoro(2-oxabicyclo[3.3.0]octane) and perfluoro(7-oxabicyclo-[4.3.0]nonane) were obtained by the fluorination of methyl cyclopentylacetate and methyl cyclohexylacetate in yields of 10.5% and 11.8% respectively. The fluorination of methyl 3-cyclopentylpropionate and methyl 3-cyclohexylpropionate afforded the new perfluoro(1-oxaspiro[4.4]nonane) and perfluoro(1-oxaspiro[4.5]-decane) as the main cyclization products in yields of 12.4% and 16.6% respectively. Several kinds of perfluorinated cyclization products having a perfluoroalkyl group at the β-carbon to oxygen were also prepared by the fluorination of α-alkyl-α-cycloalkyl-substituted acetic acids. These new fluorination products, including some perfluorocycloalkanes and perfluoroalkanoyl fluorides, have been characterized by elemental analysis and infrared, mass and ^{19}F nmr spectra.

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* 'Studies on the cyclization upon Electrochemical Fluorination', Part IV. Some results have been quoted by two of the authors (T. Abe and S. Nagase) in the monograph.

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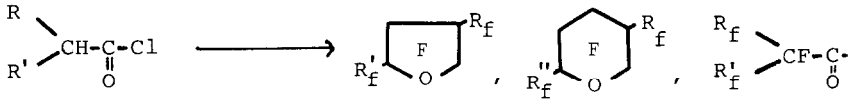
INTRODUCTION

A number of papers have reported the preparation of perfluoromonocyclic ethers by several fluorination procedures [1]. Concerning the perfluorobicyclic and perfluoromonospiro ethers except those with a fused oxirane ring, only one example, i.e. 1,4-bis(trifluoromethyl)-2,6,7-trioxaperfluorobicyclo[2.2.2]-octane, has been known previous to the start of this investigation. It was synthesized by the fluorination of 1-trifluoromethyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane with elementary fluorine [2].

However, during the course of this investigation, Tatlow and his co-workers reported the fluorination of benzofuran with cesium tetrafluorocobaltate (III), which yielded a number of partially fluorinated products together with the perfluoro(7-oxabicyclo[4.3.0]nonane) [3].

In a previous paper, we have demonstrated the fluorination of α-alkyl-substituted carboxylic acids as a synthetic approach toward the new perfluoro(2,4-dialkyloxolane)s which is based on the utility of cyclization of carboxylic acids during electrochemical fluorination [1], viz.

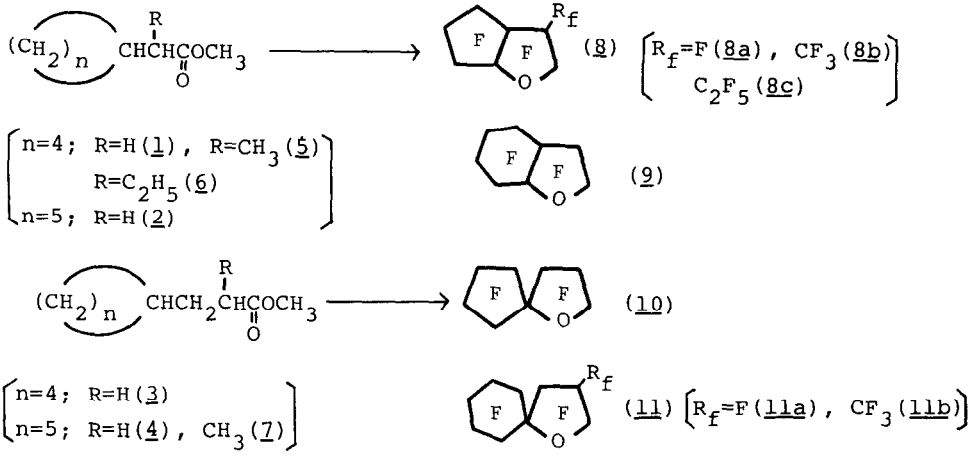


$R=CH_3$, $R'=n\text{-}C_3H_7$; $R=CH_3$, $R'=n\text{-}C_4H_9$; $R=R'=n\text{-}C_3H_7$, etc.

Therefore, we extended next the fluorination of carboxylic acids to that of the cycloalkyl-substituted ones in order to obtain new perfluorinated fused ring compounds having the ether linkage.

In this paper, we wish to report a new method for the preparation of perfluorobicyclic and perfluoromonospiro ethers by the fluorination of cycloalkyl-substituted carboxylic acids, which possesses significant features in comparison with other method; the starting materials are readily accessible and the procedures are simple.

It was found that new perfluorobicyclic and perfluoromonospiro ethers were obtained successfully from fluorinations of cycloalkyl-substituted carboxylic acid esters in fair yields according to the following general equations.



Scheme 1

The carboxylic acid esters dealt with in this paper were the following seven compounds; methyl cyclopentyl acetate (1), methyl cyclohexylacetate (2), methyl 3-cyclopentylpropionate (3), methyl 3-cyclohexylpropionate (4), methyl 2-cyclopentylpropionate (5), methyl 2-cyclopentyl-n-butyrate (6) and methyl 3-cyclohexyl-2-methylpropionate (7).

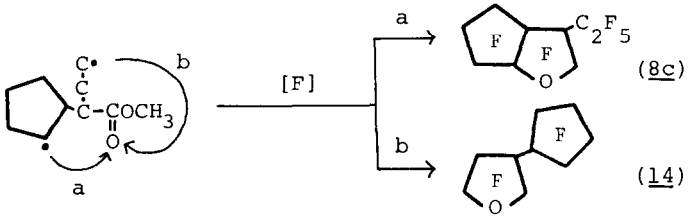
RESULTS AND DISCUSSION

All carboxylic acids used were fluorinated in the form of methyl esters, for which reactions proceeded moderately with a relatively lower and constant electrolytic voltage, compared with the cases when the corresponding carboxylic acid chlorides were fluorinated.

New cyclization products consisting of two five-membered, and five- and six-membered fused ring systems were obtained successfully by the fluorination of cycloalkyl-substituted acetic and propionic acids in fairly good yields. It was found that the type of product formed depended on the chain length of the starting cycloalkyl-substituted carboxylic ester, that is, whether acetic or propionic ones were used.
Thus, perfluoro(2-oxabicyclo[3.3.0]octane)(8a) and perfluoro(7-oxabicyclo[4.3.0]nonane)(9) were obtained from the fluorination of 1 and 2 in yields of 10.5% and 11.8% respectively.

On the other hand, the fluorination of 3 and 4 resulted in the formation of perfluoro(1-oxaspiro[4.4]nonane)(10) and perfluoro(1-oxaspiro[4.5]decane)(11a) as the main cyclization product in yields of 12.8% and 16.6% respectively, though the formation of perfluoro(2-oxabicyclo[4.3.0]nonane)(12) from the former and perfluoro(2-oxabicyclo[4.4.0]decane)(13) from the latter was most expected analogously to the fluorinations of 1 and 2. However, only a small quantities of 12 was obtained from 3, but not 13 from 4 at all. The predominant formation of 11a from 4 is an indication of a preferential formation of the less strained system.

The introduction of an another alkyl group (CH_3- or C_2H_5- group) to the α-carbon of the starting cycloalkyl-substituted carboxylic acids which should be fluorinated afforded the perfluorobicyclic and perfluoromonospiro ethers having a CF_3- or C_2F_5- group at the β-carbon to oxygen. Thus, from 5, 6 and 7, perfluoro(4-methyl-2-oxabicyclo[3.3.0]octane)(8b), perfluoro-(4-ethyl-2-oxabicyclo[3.3.0]octane)(8c) and perfluoro(3-methyl-1-oxaspiro[4.5]decane)(11b) were obtained respectively in yields of 18.8%, 14.7% and 13.8%. From 6, in addition to the expected 8c, an another kind of cyclization product, perfluoro(3-cyclopentyloxolane)(14), was produced similar to the fluorination of methyl 2-ethyl-n-valerate and 2-ethyl-n-caproyl chloride [1].



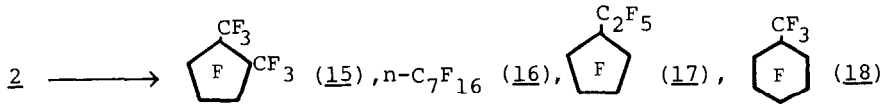
(8c)

(14)

Scheme 2

As far as the preparation of perfluoro(7-oxabicyclo[4.3.0]nonane)(9) is concerned, 2-cyclohexylethanol and cyclohexen-2-yl acetic acids (methyl ester and acid chloride) could substitute for 2 as the starting material. But, several attempted fluorinations of such compounds as phenylacetyl chloride, 2-phenylethanol, methyl phenylacetate, and benzofuran failed to give 9 because of the serious formation of either a tarry material (from the first three compounds) or a solid material.

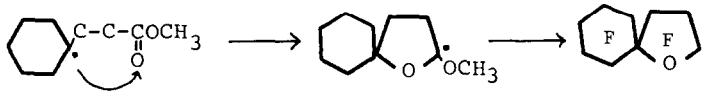
Invariably the fluorination of these cycloalkyl-substituted carboxylic esters was accompanied by the formation of perfluorocycloalkanes as the major degradation by-products, which could be removed easily by the fractional distillation from the desired cyclization products. Typical is the case of the fluorination of 2, which afforded the following three kinds of perfluorocycloalkanes and a perfluoroalkane as the cleaved products [Arranged in order of the elution time in the gas chromatogram. See the experimental section].



Scheme 3

The formation of perfluoromonospiro compounds (10, 11a and 11b) from 3-cycloalkyl-substituted propionic acids (3, 4 and 7) was rather unexpected, because there are four available C-H bond in both the cyclopentyl and cyclohexyl groups in the molecule to create a carbon radical by hydrogen abstraction by fluorine, which would contribute to the formation of 5-6 and 6-6 fused ring compounds respectively by intramolecular cyclization.

A careful inspection using models shows also that the formation of the expected bicyclic structure having a fused oxane ring is not difficult. However, the relatively stable tertiary carbon radical on the cycloalkane ring and the significant steric factors which govern the easier formation of oxolane ring might favor this cyclization. For example,



As demonstrated in a previous paper, with respect to the geminal fluorines at α-carbon to oxygen, most of the ^{19}F nmr spectra of the perfluoroalkyl-substituted oxolanes and oxanes exhibited characteristically an AB pattern at ϕ72～85 and ϕ83～93 ppm with J=158～178 Hz and at ϕ72～85 and ϕ73～93 ppm with J=130～150 Hz respectively [4]. The magnitude of the coupling constants provided useful means for differentiating between them. Likewise, ^{19}F nmr spectra of these perfluorobicyclic ethers, in most instances, exhibited direct evidence for the configuration of the newly-formed fused ring, that is, either a fused oxane or a fused oxolane ring. For example, the ^{19}F nmr spectrum of geminal fluorines at α-carbon to oxygen of 8a exhibited a typical AB pattern [ϕ80.9 and ϕ88.1 ppm, J=130 Hz] which was assignable to that of the oxolane ring. On the other hand, ^{19}F nmr spectrum of 12 showed an AB pattern at ϕ78.6 and ϕ90.8 ppm with J=158 Hz similarly to that expected for the substituted perfluorooxane ring. However, final structural determination of these perfluorobicyclic ethers including perfluoromonospiro ethers was accomplished by investigating the chlorination product which was formed by treating them with anhydrous aluminum chloride at ca. 165 °C. These results will be published later.

Among the minor cyclization by-products isolated, the most significant ones may be the β-trifluoromethoxy-substituted ones like perfluoro(3-methoxy-2-oxabicyclo[3.3.0]octane)(19) obtained from 1, perfluoro(6-methoxy-7-oxabicyclo[4.3.0]nonane)(20) obtained from 2, perfluoro(2-methoxy-1-oxaspiro[4.4]octane)(21) obtained from 3, because these products suggest the mode of cyclization of esters during fluorination, which involves a resonance stabilized intermediate radical [6]. The detailed study on the synthesis of several kinds of perfluoro(8-alkoxy-substituted 7-oxabicyclo[4.3.0]nonane)s will be published in a subsequent paper.

EXPERIMENTAL

Reagents

Cyclopentylacetic acid and 3-cyclohexylpropionic acid were purchased from Aldrich Chemicals Co., and cyclohexylacetic acid and 3-cyclohexylpropionic acid were purchased from Tokyo Kasei Co. Other carboxylic acids used were prepared by the malonic acid synthesis in an usual manner; 2-cyclopentylpropionic acid and 3-cyclohexyl-2-methylpropionic acid were prepared by the reaction of diethyl methylmalonate (Aldrich Chemicals Co.) with cyclopentyl bromide (Aldrich Chemicals Co.) and cyclohexylmethyl bromide (Tokyo Kasei Co.) respectively. The 2-cyclopentyl-n-butyric acid was prepared by the reaction of diethyl ethylmalonate (Tokyo Kasei Co.) and cyclopentyl bromide (Aldrich Chemicals Co.). All carboxylic acids were converted into methyl esters, which were purified by the fractional distillation before use. These starting materials had following boiling points; methyl cyclopentylacetate, 176.5～178.0 °C; methyl cyclohexyl acetate, 200.5～201.5 °C; 3-cyclopentyl-n-propionate, 200.5～202.0 °C; methyl 3-cyclohexyl-n-propionate, 135～136.5 °C/58 mm Hg; methyl 2-cyclopentyl-n-propionate, 86.9～87.2 °C/22 mm Hg; methyl 2-cyclopentyl-n-butyrate, 95.5～96.8 °C/18 mm Hg; methyl 2-methyl-3-cyclohexyl-n-propionate 103～104.5 °C/19 mm Hg.

Anhydrous hydrogen fluoride (Daikin Industries Co.) was better than 99.8% pure.

Apparatus

The electrolytic fluorination apparatus and operating procedures were similar to those described previously [1].

Analytical work was carried out with a Shimadzu GC-2C gas chromatograph using stainless columns (3 mm dia) packed with 30% 1,6-bis(1,1,12-trihydroperfluorodedecyloxy)hexane on Chromosorb PAW (6.4 m)(Col. A), and 26% Kel F #90 on Chromosorb PAW (3.8 m)(Col. B). For semi-preparative work, a Shimadzu GC-1C gas chromatograph was used employing stainless columns (10 mm dia) packed with 30% Silicone QF-1 on Chromosorb PAW (4.9 m) Col. C), 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane

on Chromosorb PAW (4.9 m)(Col. D), and 30% Kel F wax on Chromosorb PAW (4.9 m)(Col. E). The carrier was helium in all cases.

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

Fluorination of 1

Sample 1 (33.5 g, 0.236 mol) was charged into the cell which contained 1ℓ electrochemically purified anhydrous hydrogen fluoride, and the solution was subjected to fluorination with an anodic current density of 3.5 A/dm^2, a cell voltage of 5.3∼8.5 V, and a cell temperature of 5∼6 °C over a period of 393 min (212 Ahr).

The effluent gases from the cell were passed over NaF pellets and then condensed in a trap at -78 °C. The gaseous products which did not condensed in a trap at -78 °C were then bubbled through two consecutive polyethylene bottles containing water (for the collection of perfluorocarboxylic acids which were formed as a result of the hydrolysis of perfluorocarboxylicacid fluorides), and finally collected in traps immersed in liq. nitrogen. The products condensed in cold traps and cell drainings were subsequently analysed by GLC (Col. A). All products except new ones were identified by comparison of their infrared spectra and retention times on a gas chromatogram with those of authentic samples. In the case of new compounds, they were separated from other products by use of semi-preparative GLC, and their structure was determined on the basis of their infrared, ^{19}F nmr and mass spectra, and elemental analysis. The compounds (2.8 g) condensed at -196 °C consisted primarily of CF_4 (22), and small amounts of C_2F_6 (23) and C_3F_8 (24). The products (Compound number, g Yield)(38.5 g) condensed at -78 °C consisted of perfluoro(methylcyclopentane)(25) (10.8), perfluorocyclohexane(26) (0.7), perfluoro(cyclopentylmethyl methylether)(27) (1.6), perfluoro(2-propyloxolane)(28) (2.7), 8a (7.1), 19 (8.5), a mixture of perfluoro(cyclopentylacetyl

fluoride)(29) and perfluoro(cyclohexylcarbonyl fluoride)(30) (0.9), and unidentified (6.2). Cell drainings (6.5 g) consisted of 25 (0.3), 26 (trace), 27 (0.3), 28 (0.6), 8a (1.0), 19 (1.4), 29 + 30 (1.1) and unidentified (2.2). The acids formed in polyethylene bottles were worked up to give sodium salts (0.8 g) and were analysed by the method described previously. They consisted of 77 mol% of sodium trifluoroacetate(33), 13% of sodium pentafluoropropionate(34), 4% of sodium perfluorobutyrate(35), and 6% of sodium perfluorovalerate(36).

The composition of 29 and 30 was determined by ^{19}F nmr. On the basis of the relative areas of the absorption peaks due to -CF groups in the ^{19}F nmr spectrum of the mixture of 29 and 30, the following composition was determined; 29/30=1 : 1.26. An attempted isolation of methyl esters of 29 and 30 (31 and 32 respectively) from each other was unsuccessful.

The yields of 8a and 19 were 10.5% and 10.6% based on the sample fed respectively.

Perfluoro(cyclopentylmethyl methylether)(27)(nc) had bp 73.0~73.5 °C, $n_D^{20} < 1.28$ and d_4^{20}1.7459. IR: 1332~1337 (s), 1305 (s), 1287 (s,sh), 1262 (s,sh), 1247 (vs), 1226 (vs), 1152 (s), 1126 (m), 1053 (w), 1029 (w), 984 (ms), 936 (w), 912 (w), 876 (w), 862 (w), 840 (w), 806 (m), 739 (w), 662 (w), 602 617 (w). Mass: 347 $[M-F]^+$(1.4), 281 $C_6F_{11}^+$(6.5), 259 $C_6F_9O^+$(2.4), 247 $C_5F_9O^+$(2.0), 231 $C_5F_9^+$(4.7), 193 $C_5F_7^+$(2.3), 181 $C_4F_7^+$(8.2), 169 $C_3F_7^+$(3.7), 150 $C_3F_6^+$(2.6), 135 $C_2F_5O^+$(12.7), 131 $C_3F_5^+$ (18.8), 119 $C_2F_5^+$(5.9), 100 $C_2F_4^+$(11.9), 93 $C_3F_3^+$(4.9), 69 CF_3 (100), 50 CF_2^+(2.6), 31 CF^+(5.1). Found: C, 22.81%. Calculated for $C_7F_{14}O$: C, 22.95%.

Perfluoro(2-oxabicyclo[3.3.0]octane)(8a)(nc) had bp 74.3~75.0 °C, n_D^{20}1.2908 and d_4^{20}1.7828. IR: 1377 (w,sh), 1355 (m), 1310 (s), 1266 (m), 1239 (vs), 1224 (vs), 1206 (s,sh), 1185 (s), 1163 (m,sh), 1107 (s), 1096 (s,sh), 1087 (m,sh), 1041 (w), 1010 (m), 970 (s), 963 (m,sh), 886 (w), 860 (m), 850 (m), 638 (w,sh), 625 (w), 586 (w,sh), 575 (w). Mass: 309 $[M-F]^+$(6.1), 281 $C_6F_{11}^+$ (4.1), 262 $C_6F_{10}^+$(4.6), 259 $C_6F_9O^+$(2.5), 231 $C_5F_9^+$(14.8), 212 $C_5F_8^+$(14.8), 209 $C_5F_7O^+$(4.1), 193 $C_5F_7^+$(11.0), 181 $C_4F_7^+$(24.7), 178 $C_4F_6O^+$(37.0), 162 $C_4F_6^+$(16.7), 159 $C_4F_5O^+$(9.9), 150 $C_3F_6^+$

(3.7), 143 $C_4F_5^+$(12.0), 131 $C_3F_5^+$(100), 124 $C_4F_4^+$(6.4), 119 $C_2F_5^+$(11.4), 112 $C_3F_4^+$(6.6), 109 $C_3F_3O^+$(8.2), 100 $C_2F_4^+$(39.0), 97 $C_2F_3O^+$(7.0), 93 $C_3F_3^+$(29.0), 81 $C_2F_3^+$(3.7), 74 $C_3F_2^+$(5.2), 69 CF_3^+(52.9), 50 CF_2^+(5.8), 47 COF^+(8.0), 31 CF^+(21.5). Found: C, 25.60%. Calculated for $C_7F_{12}O$: C, 25.61%.

Perfluoro(3-methoxy-2-oxabicyclo[3.3.0]octane)(19) (nc) had bp 98.5~98.8 °C, n_D^{20}1.2922 and d_4^{20}1.8017. IR: 1351 (m), 1309 (s,sh), 1292 (s), 1273 (s,sh), 1241 (vs), 1223 (s), 1207 (s), 1187 (vs), 1169 (s,sh), 1142 (m), 1096 (m,sh), 1077 (s), 1040 (m), 1013 (s), 967 (s), 922 (m), 906 (w), 884 (w), 848 (w,sh), 837 (m), 814 (w), 756 (w,sh), 737 (w), 640 (w), 629 (w), 609 (w), 587 (w), 554 (w), 518 (w), 480 (w). Mass: 309 $[M-OCF_3]^+$ (8.3), 262 $C_7F_{12}O^+$(5.7), 231 $C_5F_9^+$(6.2), 212 $C_6F_{10}O^+$(11.9), 193 $C_5F_7^+$(7.2), 181 $C_4F_7^+$(6.0), 162 $C_4F_6^+$(8.1), 131 $C_3F_5^+$(18.8), 100 $C_2F_4^+$(10.9), 93 $C_3F_3^+$(10.3), 69 CF_3^+(100), 47 COF^+(8.3). ^{19}F nmr: $\phi(CF_3)$ 55.9(d) [$J(CF_3\text{-O-CF-O})$=10.3]; ϕ(CF) 189.0(mult); ϕ(O-CF-O) 83.0(mult). Found: C, 24.30%. Calculated for $C_8F_{14}O_2$: C, 24.37%.

^{19}F nmr data of 8a, 27, 31 and 32 are shown in Table 1.

Fluorination of 2

Sample 2 (35.2 g, 0.226 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.2~8.1 V, 5~6 °C, 420 min (226 Ahr). The product weighed 2.6 g for those collected at -196 °C, 20.7 g for those collected at -78 °C and 26.3 g for cell drainings respectively. Work-up of the products was the same as those explained for the fluorination of 1. Products trapped at -78 °C were fractionally distilled into 3 portions and these fractions and cell drainings were subsequently analysed by GLC(Col. A). Thus, the following compounds were obtained; Fraction 1, bp room temp~74.5 °C, 2.7 g [product (compound number), g Yield], perfluoro-n-pentane(37) (0.1), perfluoro-isopentane(38) (0.1), perfluorocyclopentane(39) (0.1), perfluoro-n-hexane(40) (0.1), 25 (0.3), 26 (0.4), 15 (0.6), 16 (0.1), 17 (0.3), 18 (0.4), unidentified (0.2). Fraction 2, bp 76.0~83.3 °C, 4.2 g, 15 (0.9), 16 (0.1), 17 (1.1), 18 (1.7), unidentified (0.4). Residue, 12.3 g, 15 (0.1), 17 (0.8), 18 (0.8), 9 (3.6), perfluoro(3-cyclopentylpropionyl fluoride)(41) (0.5),

perfluoro(cyclohexylacetyl fluoride)(42) (0.7), unidentified (5.8), Cell drainings, 26.3 g, 15 (0.3), 17 (0.8), 18 (1.0), 9 (6.4), 41 (1.2), 42 (2.1), 20 (3.8), unidentified (10.7). The yields of 9 and 20 were 11.8% and 4.3% respectively. The compounds in the -196 °C trap were primarily 22 and small amounts of 23 and 24. The sodium salts of acids (0.5 g) consisted of 36 (54 mol%), 37 (31), 38 (9) and 39 (5).

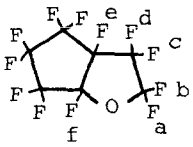
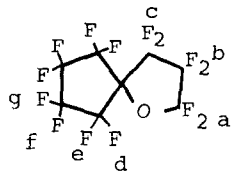
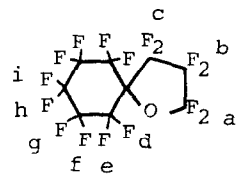
Perfluoro(7-oxabicyclo[4.3.0]nonane)(9) had bp 98.3~98.7 °C, n_D^{20}1.2991 and d_4^{20}1.8412. IR: 1366 (m), 1308 (m), 1287 (s), 1249 (vs), 1232 (vs,sh), 1189 (vs), 1177 (s,sh), 1160 (m), 1134 (w), 1086 (vs), 1065 (ms), 1027 (m), 1000 (ms), 965 (s), 866 (w), 838 (ms), 813 (w), 657~672 (w), 628 (w), 607 (w), 570 (w), 532 (w), 510 (w), 466 (w). Mass: 359 $[M-F]^+$(5.8), 331 $C_7F_{13}^+$(3.7), 293 $C_7F_{11}^+$(2.2), 281 $C_6F_{11}^+$(2.5), 243 $C_6F_9^+$(22.7), 231 $C_5F_9^+$(15.1), 212 $C_5F_8^+$(43.6), 193 $C_5F_7^+$(13.5), 181 $C_4F_7^+$(27.6), 162 $C_4F_6^+$(11.0), 143 $C_4F_5^+$(12.0), 131 $C_3F_5^+$(100), 119 $C_2F_5^+$(14.7), 100 $C_2F_4^+$(30.4), 97 $C_2F_3O^+$(5.5), 93 $C_3F_3^+$(19.9), 69 CF_3^+(66.6), 50 CF_2^+(2.8), 47 COF^+(5.5), 31 CF^+(9.2). ^{19}F nmr: ϕ(α CF_2) 79.5 and 84.6 (J_{AB}=127 Hz); ϕ(CF) 191.7(mult). Found: C, 25.28%. Calculated for $C_8F_{14}O$: C, 25.40%.

Perfluoro(6-methoxy-7-oxabicyclo[4.3.0]nonane)(20) (nc) had bp 114.5~115.3 °C, n_D^{20}1.3005 and d_4^{20}1.8569. IR: 1355 (w,sh), 1315 (ms), 1282~1297 (s), 1237~1250 (s~vs), 1163~1186 (s~vs), 1183 (ms), 1053 (s), 1025 (w), 1002 (ms), 966 (s), 901 (m), 833 (m), 818 (m), 695 (w), 630~655 (w), 598 (w), 510 (w). Mass: 359 $[M-OCF_3]^+$(5.6), 281 $C_6F_{11}^+$(2.6), 243 $C_6F_9^+$(10.3), 212 $C_5F_8^+$(20.2), 193 $C_5F_7^+$(5.3), 181 $C_4F_7^+$(4.5), 162 $C_4F_6^+$(4.0), 143 $C_4F_5^+$(3.6), 131 $C_3F_5^+$(15.7), 100 $C_2F_4^+$(5.4), 93 $C_3F_3^+$(4.5), 69 CF_3^+(100), 47 COF^+(5.6), 31 CF^+(2.2). ^{19}F nmr: ϕ(CF_3) 56.0 (d) [J(CF_3-O-CF-O)=10.4 Hz]; ϕ(O-CF-O) 80.4(mult); ϕ(CF) 191.2 (mult). Found: C, 24.19%. Calculated for $C_9F_{16}O_2$: C, 24.32%.

Perfluoro(3-cyclopentylpropionyl fluoride)(41) (nc) showed the following infrared spectrum. IR: 1887 ν(c=o)(s), 1316 (s), 1274 1279 (s), 1251 (vs), 1224 (vs), 1179 (s), 1141 (m), 1029 1047 (m), 988 (m), 971 (m), 871 (w), 801 (w), 785 (w), 729 739 (w), 709 (w), 674 (w), 607 (w), 569 (w).

TABLE 1

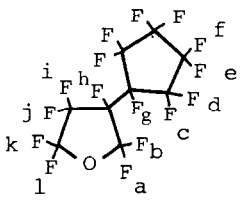
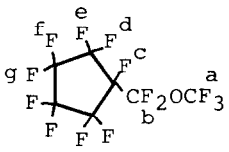
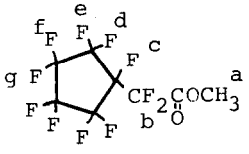
^{19}F nmr spectra of 8a, 10, 11a, 14, 27, 31, 32, 43, 44, 46, 48, 50, 52 and 54

Compd	Formula		Chemical shift[a,b]	J (Hz)[b]
8a		a	80.9]J_{AB}	a-b=130
		b	88.1]	c-d=258
		c	116.7]J_{AB}	
		d	127.6]	
		e	190.7	
		f	129.0	
10		a	84.4	d-e=264
		b	123.0	f-g=258
		c	134.3	
		d	123.7]J_{AB}	
		e	131.1]	
		f	125.1]J_{AB}	
		g	130.6]	
11a		a	83.5	d-e=290
		b	117.4	f-g=290
		c	124.4	h-i=220
		d	]J_{AB}	
		e	]	
		f	]J_{AB}	
		g	]	
		h	]J_{AB}	
		i	]	

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

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

Table 1 (cont.)

14		a	72.9	a-b=144
		b	82.6	c-d=268
		c	121.9	e-f=258
		d	128.7	k-l=131
		e	128.3	f-h=26
		f	132.2	
		g	179.2	
		h	183.4	
		i		
		j		
		k	81.4	
		l	90.3	
27		a	55.9	a-b=9.2
		b	77.9	d-e=270
		c	184.9	f-g=272
		d	125.2	
		e	130.2	
		f	130.4	
		g	133.1	
31		a	δ=3.98	a-b=5.9
		b	112.3	b-d=18.6
		c	183.2	d-e=270
		d	124.2	f-g=257
		e	129.1	
		f	129.8	
		g	133.0	

(cont. overleaf)

Table 1 (cont.)

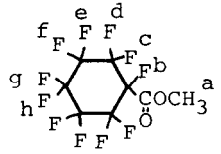
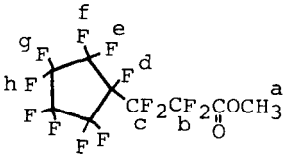
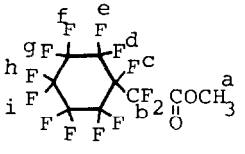
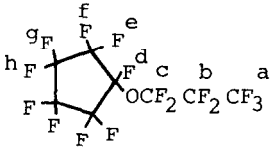
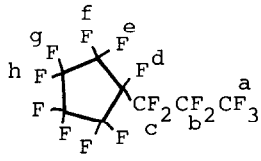
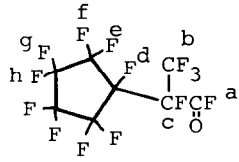
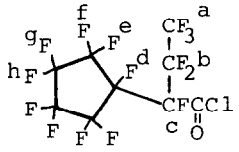
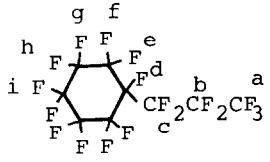
32		a	δ=4.01	b-c=16
		b	179.5	b-d=16
		c	118.2] J_{AB}	c-d=292
		d	132.2]	e-f=280
		e	123.4] J_{AB}	g-h=286
		f	139.5]	
		g	122.7] J_{AB}	
		h	142.0]	
43		a	δ=3.97	e-f=274
		b	116.2	g-h=260
		c	117.9	
		d	185.1	
		e	123.1] J_{AB}	
		f	128.7]	
		g	128.5] J_{AB}	
		h	132.2]	
44		a	δ=3.92	d-e=296
		b	110.6	f-g=286
		c	186.5	h-i=296
		d	119.4] J_{AB}	
		e	131.0]	
		f	122.8] J_{AB}	
		g	140.3]	
		h	124.4] J_{AB}	
		i	142.5]	
46		a	82.2	e-f=262
		b	137.2	g-h=258
		c	82.9	
		d	130.2	
		e	125.1] J_{AB}	
		f	133.9]	
		g	129.6] J_{AB}	
		h	135.0]	

Table 1 (cont.)

48		a	81.6	a-c=11.0
		b	125.4	e-f=274
		c	116.8	g-h=258
		d	185.3	
		e	123.3]J_{AB}	
		f	129.0]	
		g	129.8]J_{AB}	
		h	133.0]	
50		a	-33.4	e-f=272
		b	72.7	g-h=258
		c	181.7	g-c=36
		d	176.9	
		e	120.8]J_{AB}	
		f	130.3]	
		g	126.1]J_{AB}	
		h	131.0]	
52		a	79.6	a-c=13.1
		b	117.3	g-c=63
		c	162.2	e-f=270
		d	178.6	g-h=258
		e	119.6]J_{AB}	
		f	127.6]	
		g	127.7]J_{AB}	
		h	131.9]	
54		a	81.4	a-c=11.0
		b	124.3	a-d=1.9
		c	111.1	g-h=284
		d	179.7	i-j=284
		e		
		f	]J_{AB}	
		g		
		h	]J_{AB}	
		i		
		j	]J_{AB}	

Perfluoro(cyclohexylacetyl fluoride)(42)(nc) showed the following infrared spectrum. IR: 1888 ν(c=o)(s) 1298~1318 (s), 1258 (vs), 1217 (vs), 1200 (vs), 1168 (m), 1136 (m), 1059 (m), 1045 (w,sh), 1014 (ms), 970 (vs), 855 (w), 845 (w), 820 (m), 760 (w), 736 (w), 676 (w), 623~635 (w), 500 (w), 465 (w).

Further characterization of 3a and 42 was by conversion to methyl esters by treating them with methanol at room temperature.

Methyl perfluoro(3-cyclopentylpropionate)(43)(nc) had bp 152.5~153.5 °C, n_D^{20}1.3233 and d_4^{20}1.7212. IR(capillary film): 2970 (w), 1789 ν(c=o)(vs), 1443 (m), 1310~1327 (s), 1250~1280 (s), 1195~1220 (vs), 1168 (s,sh), 1142 (s), 1112 (m), 1080 (w), 1050 (ms), 1032 (ms), 1017 (w), 990 (w), 968 (s), 938 (w), 868 (m), 851 (w), 823 (w), 800 (w), 788 (ms), 776 (m), 750 (w), 698 (w), 635 (w), 605~615 (w), 567 (w). Mass: 371 $[M-F]^+$(3.8), 343 $C_8F_{13}^+$(5.6), 331 $C_7F_{13}^+$(5.3), 281 $C_6F_{11}^+$(3.7), 243 $C_6F_9^+$(5.7), 231 $C_5F_9^+$(5.8), 193 $C_5F_7^+$(10.7), 181 $C_4F_7^+$(9.0), 162 $C_4F_6^+$(6.3), 143 $C_4F_5^+$(7.0), 131 $C_3F_5^+$(23.6), 119 $C_2F_5^+$(15.0), 100 $C_2F_4^+$(16.9), 93 $C_3F_3^+$(13.1), 69 CF_3^+(28.6), 59 $CO_2CH_3^+$(100). Found: C, 27.15%. Calculated for $C_9H_3F_{13}O_2$: C, 27.69%.

Methyl perfluorocyclohexylacetate (44)(nc) had bp 151.3 152.0 °C, n_D^{20}1.3266 and d_4^{20}1.7530. IR(capillary film): 2970 (w), 1787 ν(c=o)(vs), 1442 (m), 1318 (s), 1190~1273 (vs), 1175 (s,sh), 1160 (s,sh), 1139 (m), 1081 (m), 1055 (w), 1016 (s), 967 (vs), 950 (m,sh), 864 (w), 852 (m), 801 (ms), 788 (w), 774 (w), 695 (w), 634 (m), 627 (w), 502 (w), 465 (w). Mass: 371 $[M-F]^+$(4.2), 343 $C_8F_{13}^+$(6.3), 331 $C_7F_{13}^+$(5.3), 281 $C_6F_{11}^+$(4.0), 243 $C_6F_9^+$(7.4), 193 $C_5F_7^+$(6.3), 181 $C_4F_7^+$(9.5), 162 $C_4F_6^+$(8.5), 143 $C_4F_5^+$(6.3), 131 $C_3F_5^+$(27.6), 100 $C_2F_4^+$(10.3), 93 $C_3F_3^+$(12.8), 69 CF_3^+(41.9), 59 $CO_2CH_3^+$(100). Found: C, 27.65%. Calculated for $C_9H_3F_{13}O_2$: C, 27.69%.

^{19}F nmr data of 43 and 44 are shown in Table 1.

Fluorination of 3

Sample 3 (35.5 g, 0.228 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.1~8.1 V, 5~6 °C, 281 min (216 Ahr).

The amounts of the products were 1.8 g for those collected at -196 °C, 28.3 g for those collected at -78 °C and 28.0 g for the cell drainings respectively. Work-up of the products was almost the same as explained for the fluorination of 1.

Thus, the following compounds were obtained; product in the -78 °C trap, 28.3 g, perfluoro-n-butane (45)(0.4), 39 (0.7), 17 (6.7), 18 (1.2), 10 (3.4), perfluoro(cyclopentyl-n-propyl-ether)(46) (1.6), 9 + 12 (2.5), 41 (0.4), unidentified (11.4). Cell drainings, 28.3 g, 17 (3.0), 18 (0.6), 10 (7.3), 46 (2.3), 9 + 12 (4.8), 21 (2.5), 41 (0.7), 42 (0.8), unidentified (6.3).

Among these products, a mixture of 9 and 12 was isolated from other products by GLC(Col. C and D) and were characterized spectroscopically. Based on the relative areas of absorption peaks due to the -CF groups (ϕ185.6 for 12 and ϕ191.7 for 9, respectively) in the ^{19}F nmr spectrum of the mixture of 12 and 9, the consistuent ratio was determined to be 12/9= 1 : 0.68. The yields of 10 and 21 were 12.4% and 2.5% respectively. The compounds in the -196 °C trap consisted primarily of 22 and small amounts of 23 and 24. The sodium salts of acids (0.5 g) consisted of 36 (30 mol%), 37 (62), 38 (4) and 39 (5).

Perfluoro(1-oxaspiro[4.4]octane)(10)(nc) had bp 91.0~92.3 °C, n_D^{20}1.2949 and d_4^{20}1.8099. IR: 1385 (m), 1316 (s), 1295 (m,sh) 1255 (ms), 1220 (vs), 1200 (s), 1130 (s), 1107 (s), 1065 (m), 1019 (ms), 973 (s), 864 (w), 810 (s), 656 (w), 613 (w), 593 (w), 570 (w), 545 (m). Mass: 378 M^+(3.6), 359 $[M-F]^+$(20.2), 309 $C_7F_{11}O^+$(5.1), 259 $C_6F_9O^+$(60.2), 243 $C_6F_9^+$(29.3), 209 $C_5F_7O^+$ (13.3), 193 $C_5F_7^+$(24.4), 181 $C_4F_7^+$(33.2), 143 $C_5F_5^+$(23.0), 131 $C_3F_5^+$(39.7), 109 $C_3F_3O^+$(29.8), 100 $C_2F_4^+$(100), 93 $C_3F_3^+$(39.7), 69 CF_3^+(86.4), 50 CF_2^+(12.3), 31 CF^+(27.8). Found: C, 25.41%. Calculated for $C_8F_{14}O$: C, 25.40%.

Perfluoro(cyclopentyl n-propylether)(46)(nc) had bp 93.0 ~93.5 °C, n_D^{20}<1.28 and d_4^{20}1.7581. IR: 1346 (ms), 1322 (s), 1283 (ms), 1248 (vs), 1222 (vs), 1181 (ms), 1160 (vs), 1138 (ms), 1076 (w), 1043 (w), 1006 (vs), 991 (s), 977 (ms), 894 (w), 791 (w), 738~751 (m), 701 (w), 615 (m), 564 (w), 537 (m). Mass: 397 $[M-F]^+$(4.0), 297 $C_6F_{11}O^+$(6.1), 231 $C_5F_9^+$(18.5), 181 $C_4F_7^+$ (20.0), 169 $C_3F_7^+$(62.4), 131 $C_3F_5^+$(52.6), 119 $C_2F_5^+$(12.6), 100 $C_2F_4^+$(22.6), 93 $C_3F_3^+$(9.5), 69 CF_3^+(100). Found: C, 23.00%. Calculated for $C_8F_{16}O$: C, 23.08%.

Perfluoro(2-methoxy-1-oxaspiro[4.4]octane)(21)(nc) had bp 106.5~107.7 °C, n_D^{20}1.2953 and d_4^{20}1.8500. IR: 1368~1383 (w), 1318 (s), 1288 (s), 1246 (vs), 1211 (s~vs), 1195 (s),

1177 (m), 1149 (m), 1119 (m), 1103 (m), 1081 (s), 1023 (m), 991 (m), 974 (ms), 881 (w), 804 (m), 736 (w), 616 (w), 596 (w), 567 (w), 546 (w). Mass: 359 $[M-OCF_3]^+$(7.0), 309 $C_7F_{11}O^+$(2.7), 281 $C_6F_{11}^+$(2.6), 243 $C_6F_9^+$(27.9), 231 $C_5F_9^+$(4.0), 193 $C_5F_7^+$(6.2), 181 $C_4F_7^+$(7.9), 131 $C_3F_5^+$(20.8), 119 $C_2F_5^+$(4.7), 100 $C_2F_4^+$(17.8), 93 $C_3F_3^+$(8.5), 69 CF_3^+(100). ^{19}F nmr: $\phi(CF_3)$ 55.9(d) [$J(CF_3-F)$= 10.2 Hz]; ϕ(CF) 83.3(mult). Found: C, 24.23%. Calculated for $C_9F_{16}O_2$: C, 24.32%.

^{19}F nmr data of 10 and 46 are shown in Table 1.

Fluorination of 4

Sample 4 (34.9 g, 0.205 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.1～8.0 V, 5～6 °C, 439 min (236 Ahr).

The products weighed 2.2 g for those collected at -196 °C, 11.1 g for those collected at -78 °C and 51.9 g for cell drainings respectively. Work-up of the products was the same as explained for the fluorination of 2. Products collected in the -78 °C trap and cell drainings were subjected to distillation and were separated into few fractions before GC analysis respectively. Distillation of the product collected at -78 °C; Fraction 1, room temp～97.9 °C, 1.5 g, 45 (trace), 37 (0.1), 38 (trace), 25 (0.6), 26 (0.4), 15 (trace), 16 (trace), unidentified (0.4). Fraction 2, 99.5～105.5 °C, 3.2 g, 15 (trace), 17 (0.2), 18 (0.1), perfluoro(1-methyl-2-ethylpentane)(47) (0.7), perfluoro(n-propylcyclopentane)(48) (1.0), perfluoro(ethylcyclohexane)(49) (0.8), unidentified (0.4). Residue, 4.9 g, 47 (0.1), 48 (0.6), 47 (0.5), 11a (1.6), unidentified (2.1). Distillation of cell drainings; Fraction 1, bp room temp～112.9 °C, 3.1 g, 17 (trace), 18 (trace), 47 (0.6), 48 (1.0), 49 (0.9), 11a (0.1), unidentified (0.5). Fraction 2, bp 114.5～127.5 °C, 14.2 g, 48 (0.7), 49 (0.5), 11a (7.3), unidentified (5.7), Fraction 3, bp 128.5～133.5 °C, 7.4 g, 11a (3.1), unidentified (4.3). Residue, 17.5 g, 11a (2.4), unidentified (15.1). The yield of 11a was 16.7%. The compounds in the -196 °C trap were mostly 22 and small amounts of 23 and 24. The sodium salts of acids (1.0 g) consisted of 36 (27 mol%), 37 (67), 38 (4) and 39 (2).

Perfluoro(n-propylcyclopentane) (48) (nc) had bp 94.5～95.0 °C, n_D^{20}1.2805 and d_4^{20}1.8057. IR: 1343 (s,sh), 1325 (s), 1216～1278 (vs), 1176 (m), 1144 (s), 1108 (w), 1068 (w,sh), 1048 (ms), 1033 (ms,sh), 1005 (w), 985 (s), 950 (m), 901 (w), 873 (m), 812 (w), 783 (m), 741 (m), 725 (s), 635 (w), 663 (w), 615 (w), 601 (w), 568 (w), 523 (w). Mass: 381 $[M-F]^+$(4.1), 331 $C_7F_{13}^+$(2.1), 281 $C_6F_{11}^+$(15.6), 243 $C_6F_9^+$(2.4), 231 $C_5F_9^+$(10.5), 219 $C_4F_9^+$ (3.5), 193 $C_5F_7^+$(4.2), 181 $C_4F_7^+$(18.1), 169 $C_3F_7^+$(15.2), 162 $C_4F_6^+$(3.1), 150 $C_3F_6^+$(2.4), 143 $C_4F_5^+$(4.0), 131 $C_3F_5^+$(31.8), 119 $C_2F_5^+$(26.4), 100 $C_2F_4^+$(14.9), 93 $C_3F_3^+$(7.5), 69 CF_3^+(100), 50 CF_2^+(1.9), 31 CF^+(6.6). Found: C, 24.03%. Calculated for C_8F_{16}: C, 24.00%.

Perfluoro(1-oxaspiro[4.5]decane) (11a) (nc) had bp 112.2～112.5 °C, n_D^{20}1.3005 and d_4^{20}1.8579. IR: 1372 (w), 1314～1323 (s), 1294 (s), 1196～1256 (vs), 1164 (w), 1131 (m), 1109 (ms), 1084 (ms), 1066 (m), 1049 (m), 1018 (m), 973 (s), 936 (w), 878 (w), 806 (m), 785 (w), 764 (w), 736 (w), 671 (w), 636 (w), 613 (w), 558 (w), 516 (w). Mass: 409 $[M-F]^+$(4.8), 309 $C_7F_{11}O^+$(3.4), 293 $C_7F_{11}^+$(12.8), 259 $C_6F_6O^+$(12.4), 243 $C_6F_9^+$(10.1), 231 $C_5F_9^+$ (4.8), 193 $C_5F_7^+$(9.6), 181 $C_4F_7^+$(17.5), 169 $C_3F_7^+$(18.8), 150 $C_3F_6^+$(36.5), 143 $C_4F_5^+$(8.0), 131 $C_3F_5^+$(60.4), 119 $C_2F_5^+$(15.5), 112 $C_3F_4^+$(5.3), 109 $C_3F_3O^+$(8.0), 100 $C_2F_4^+$(77.5), 93 $C_3F_3^+$(15.6), 69 CF_3^+(100), 50 CF_2^+(5.0), 43 C_2F^+(5.1), 31 CF^+(10.1). Found: C, 25.15%. Calculated for $C_9F_{16}O$: C, 25.23%.

^{19}F nmr data of 11a and 48 are shown in Table 1.

Fluorination of 5

Sample 5 (34.9 g, 0.224 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.5～9.0 V, 5～6 °C, 447 min (239 Ahr).

The product weighed 4.5 g for that collected at -196 °C, 25.4 g for that collected at -78 °C and 24.8 g for cell drainings respectively. Work-up of the products was the same as explained for the fluorination of 1. Thus, the following compounds were obtained; products in the -78 °C trap, 39 (0.9), 25 (0.4), 26 (0.2), 17 (2.9), 18 (0.6), 8a (0.3), 29 + 30 (0.6), 8b (8.0), perfluoro(2-cyclopentylpropionyl fluoride) (50) (4.5), unidentified (7.0). Cell drainings, 17 (0.6), 8b (7.9), 50 (5.1), unidentified (11.2). The yield of 8b was 18.8%. The compounds

in the -196 °C trap were mostly 22 and small amounts of 23 and 24 The sodium salts of acids (0.6 g) consisted of 36 (35 mol%), 37 (61), 38 (4) and 39 (1).

Perfluoro(4-methyl-2-oxabicyclo[3.3.0]octane) (8b) (nc) had bp 94.0～94.7 °C, n_D^{20}1.2937 and d_4^{20}1.8122. IR: 1354 (m,sh), 1336 (ms), 1298 (s), 1257 (vs), 1239 (vs), 1223 (vs), 1206 (s), 1188 (m), 1176 (m), 1160 (ms), 1119 (ms), 1063 (m), 1055 (s), 1000 (m), 955 (s), 873 (w), 828 (ms), 810 (w,sh), 736 (m), 624 (w), 543 (w), 518 (w). Mass: 359 $[M-F]^+$(13.8), 281 $C_6F_{11}^+$(15.2), 243 $C_6F_9^+$(19.7), 231 $C_5F_9^+$(7.7), 228 $C_5F_8O^+$(17.2), 212 $C_5F_8^+$ (9.5), 193 $C_5F_7^+$(16.6), 181 $C_4F_7^+$(32.6), 162 $C_4F_6^+$(9.3), 159 $C_4F_5O^+$(11.0), 143 $C_4F_5^+$(12.9), 131 $C_3F_5^+$(80.2), 119 $C_2F_5^+$(12.1), 100 $C_2F_4^+$(31.0), 93 $C_3F_3^+$(27.6), 69 CF_3^+(100), 47 COF^+(10.1), 13 CF^+(14.5). ^{19}F nmr: ϕ(α CF_2) 76.2(mult); ϕ(CF_3) 74.7(mult); ϕ(CF-CF_3) 178.0(mult); ϕ(CF) 188.0(mult). Found: C, 25.33%. Calculated for $C_8F_{14}O$: C, 25.40%.

Perfluoro(2-cyclopentylpropionyl fluoride) (50) (nc) had bp 98.0～98.7 °C, n_D^{20}1.2960 and d_4^{20}1.7940. IR: 1888 ν(c=o)(m), 1877 (m), 1370 (w), 1345 (w), 1314 (ms), 1283 (m,sh), 1250 (vs), 1188 (vs), 1150 (m), 1126 (w), 1046～1075 (w), 1013 (ms), 970 (m,sh), 955 (m), 863 (w), 815 (ms), 755 (w), 735 (w), 705 (w), 692 (w), 637 (w), 615 (w), 571 (w), 535 (w). Mass: 359 $[M-F]^+$ (3.1), 331 $[M-COF]^+$(7.5), 293 $C_7F_{11}^+$(3.3), 281 $C_6F_{11}^+$(4.2), 259 $C_6F_9O^+$(7.8), 243 $C_6F_9^+$(11.1), 231 $C_5F_9^+$(16.8), 193 $C_5F_7^+$ (12.2), 181 $C_3F_8^+$(36.6), 162 $C_4F_6^+$(9.0), 147 $C_3F_5O^+$(11.8), 131 $C_3F_5^+$(90.4), 119 $C_2F_5^+$(17.0), 100 $C_2F_4^+$(32.2), 93 $C_3F_3^+$(25.3), 69 CF_3^+(100), 47 COF^+(27.9), 43 C_2F^+(50.5), 31 CF^+(15.2). Found: C, 25.45%. Calculated for $C_8F_{14}O$: C, 25.40%.

^{19}F nmr data of 50 are shown in Table 1.

Fluorination of 6

Sample 6 (34.0 g, 0.200 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.3～8.5 V, 5～6 °C, 483 min (238 Ahr).

The products weighed 4.5 g for those collected at -196 °C and 10.9 g for those at -78 °C and 38.1 g for cell drainings respectively. Work-up of the products was the same as explained for the fluorination of 2. Thus, the following compounds

were obtained; distillation of the product obtained in the -78 °C trap, Fraction 1, bp room temp ~ 90.0 °C, 0.8 g, 37 (trace) 38 (trace), 39 (trace), 25 (0.3), 8a (trace), unidentified (0.4). Fraction 2, bp 90.5 ~ 119.5 °C, 3.1 g, 8a (0.2), 29 + 30 (0.2), 48 (1.2), 49 (0.2), 8c (0.2), unidentified (1.1), Residue, 5.8 g, 48 (0.3), 8c (1.8), perfluoro(2-cyclopentylbytyryl fluoride) (51) + 14 (1.8), unidentified (1.9). Cell drainings, 38.1 g, 48 (1.7), 8c (10.6), 51 + 14 (9.3), unidentified (16.5). The compounds in the -196 °C trap were mostly 22 and small amounts of 23 and 24. The sodium salts of acids (1.0 g) consisted of 36 (63 mol%), 37 (13) and 38 (24).

On the basis of the relative areas of the absorption peaks due to -CF group (ϕ175.9 for 51 and ϕ179.2 for 14, respectively) in the ^{19}F nmr spectrum of the combined sample mixture of 51 and 14 from Residue and Cell drainings, the following composition was determined: 51/14 = 62 : 38. Its mixture could not be resolved by GLC at all. Hence it was treated with anhydrous $AlCl_3$ at such a reaction condition as only the acid fluoride would change into the corresponding acid chloride (52), which was easily separated from the former.

The reaction of a mixture of 14 and 51 with anhydrous $AlCl_3$

In a 30 ml Hoke bomb, 3.4 g of a mixture of 14 and 51, and 1.0 g of anhydrous $AlCl_3$ were held at 100 °C for 23 hr. The products were separated by trap-to-trap distillation. The compounds (3.25 g) retained at -78 °C consisted of 14 and pentadecafluoro-2-cyclopentylpropionyl chloride (52) in a ratio of 14/52 = 38 : 62 (Col. B).

Perfluoro(4-ethyl-2-oxabicyclo[3.3.0]octane) (8c) (nc) had bp 115.5 ~ 115.8 °C, n_D^{20} 1.2991 and d_4^{20} 1.8497. IR: 1355 (ms), 1328 (w), 1303 (s), 1278 (s,sh), 1226 ~ 1251 (vs), 1209 (s), 1188 (m,sh), 1173 (m,sh), 1156 (s), 1136 (m), 1126 (w,sh), 1105 (w), 1088 (w), 1064 (w), 1036 (m), 1001 (m), 983 (w), 973 (w,sh), 938 (m), 900 (m), 870 (w), 818 (m), 803 (m), 743 (ms), 625 (w), 525 (w). Mass: 409 $[M-F]^+$(15.5), 343 $C_8F_{13}^+$(7.0), 331 $C_7F_{13}^+$ (18.3), 293 $C_7F_{11}^+$(7.3), 278 $C_6F_{10}O^+$(18.3), 262 $C_6F_{10}^+$(7.5), 243 $C_6F_9^+$(22.5), 231 $C_5F_9^+$(18.3), 193 $C_5F_7^+$(16.2), 181 $C_4F_7^+$ (32.6), 159 $C_4F_5O^+$(15.5), 143 $C_4F_5^+$(12.4), 131 $C_3F_5^+$(84.4), 119

$C_2F_5^+$(32.3), 100 $C_2F_4^+$(37.6), 93 $C_3F_3^+$(22.9), 69 CF_3^+(100), 47 COF^+(12.0), 31 CF^+(9.7). ^{19}F nmr: ϕ(α CF_2) 74.5(mult); ϕ(CF_3) 81.4(mult); ϕ(-CF-C_2F_5) 178.0(mult); ϕ(CF) 188.0(mult). Found: C, 25.18%. Calculated for $C_9F_{16}O$: C, 25.23%.

Perfluoro(3-cyclopentyloxolane) (14) (nc) had bp 121.5～122.0 °C, n_D^{20}1.3032 and d_4^{20}1.8671. IR: 1373 (m,sh), 1343 (m,sh), 1293 (s,sh), 1227～1261 (vs), 1198 (s,sh), 1178 (s,sh), 1135 (ms), 1081 (ms), 1035 (ms), 1011 (w), 976 (m), 936 (m), 853 (w), 818 (w), 807 (w), 790 (w), 766 (ms), 748 (w), 730 (w), 695 (w), 673 (w), 618 (w), 575 (w), 543 (w), 515 (w). Mass: 409 $[M-F]^+$(4.5), 381 $C_8F_{15}^+$(5.2), 343 $C_8F_{13}^+$(4.0), 331 $C_7F_{13}^+$(3.8), 312 $C_7F_{12}^+$ (9.3), 293 $C_7F_{11}^+$(9.5), 262 $C_6F_{10}^+$(5.8), 243 $C_5F_{10}^+$(100), 231 $C_5F_9^+$(11.8), 212 $C_5F_8^+$(5.8), 193 $C_5F_7^+$(58.3), 181 $C_4F_7^+$(14.0), 162 $C_4F_6^+$(10.0), 150 $C_3F_6^+$(8.7), 143 $C_4F_5^+$(16.8), 131 $C_3F_5^+$(71.8), 119 $C_2F_5^+$(17.0), 100 $C_2F_4^+$(28.9), 93 $C_3F_3^+$(24.4), 69 CF_3^+(80.6), 47 COF^+(6.5), 31 CF^+(10.2). Found: C, 25.11%. Calculated for $C_9F_{16}O$: C, 25.23%.

Pentadecafluoro-2-cyclopentylpropionyl chloride (52) (nc) had bp 138.0～138.5 °C, n_D^{20}1.3263 and d_4^{20}1.8371. IR(capillary film): 1785 ν(c=o)(s), 1372 (w), 1340 (s), 1311 (s), 1197～1257 (vs～s), 1150 (ms), 1102 (ms), 1085 (m), 1045 (ms,sh), 1026 (s), 980 (ms), 947 (w), 882 (s), 867 (w), 843 (w), 798 (m), 784 (w), 752 (s), 729 (s), 672 (w), 654 (w), 618 (w), 597 (w), 553 (m), 542 (w), 523 (w). Mass: 425 $[M-F]^+$(2.9), 409 $[M-Cl]^+$ (11.4), 381 $C_8F_{15}^+$(7.7), 281 $C_6F_{11}^+$(4.7), 243 $C_6F_9^+$(8.4), 231 $C_5F_9^+$(9.3), 193 $C_5F_7^+$(8.7), 181 $C_4F_7^+$(13.2), 143 $C_4F_5^+$(8.0), 131 $C_3F_5^+$(2.4), 119 $C_2F_5^+$(24.1), 100 $C_2F_4^+$(11.5), 93 $C_3F_3^+$(13.2), 69 CF_3^+(53.9), 63 $COCl^{35+}$(100), 31 CF^+(6.6). Found: C, 24.29%. Calculated for $C_9F_{15}OCl$: C, 24.30%.

^{19}F nmr data of 14 and 52 are shown in Table 1.

Fluorination of 7

Sample 7 (33.9 g, 0.184 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.7～8.1 V, 5～6 °C, 426 min (228 Ahr).

The products weighed 2.9 g for those collected at -196 °C, 5.1 g for those collected at -78 °C and 49.3 g for cell drainings respectively. Work-up of the products was the same as

explained for the fluorination of 1. Thus, the following compounds were obtained; products obtained in the -78 °C trap, 5.1 g, 37 (0.4), 38 (0.1), 25 (0.6), 26 (0.9), 17 (0.2), 18 (0.2), 11b (0.6), unidentified (2.1). Cell drainings, 49.3 g, perfluoro(n-butylcyclopentane)(53) (1.6), perfluoro(n-propylcyclohexane) (54) (0.9), 11b (11.3), perfluoro(2-cyclohexylmethylpropionyl fluoride)(55) (11.2), unidentified (24.3). The yield of 11b was 13.4%. The compounds in the -196 °C trap were mostly 22 and small amounts of 23 and 24. The sodium salts of acids (0.4 g) consisted of 36 (41 mol%), 37 (48), 38 (8) and 39 (3).

Perfluoro(n-butylcyclopentane)(53) (nc) had bp 97.0～99.5 °C and n_D^{20}1.2937. IR: 1348 (m), 1325 (m), 1319 (m,sh), 1288 (s), 1272 (s,sh), 1257 (vs), 1245 (vs), 1220 (vs), 1195 (s), 1158 (m), 1143 (m), 1124 (m), 1097 (w), 1084 (w,sh), 1057 (w), 1029 (vs), 1012 (w,sh), 977 (m), 957 (w,sh), 931 (w), 852 (w), 817 (w), 798 (w), 778 (w), 743 (w), 723 (s), 637 (m), 618 (w), 595 (w), 532 (w), 528 (w), 499 (w), 464 (w). Mass: 431 $[M-F]^+$(4.2), 381 $C_8F_{15}^+$(5.8), 331 $C_7F_{13}^+$(6.6), 281 $C_6F_{11}^+$(6.0), 262 $C_6F_{10}^+$(4.8), 243 $C_6F_9^+$(5.2), 231 $C_5F_9^+$(7.2), 181 $C_4F_7^+$(13.0), 169 $C_3F_7^+$(23.1), 131 $C_3F_5^+$(27.3), 119 $C_2F_5^+$(22.7), 100 $C_2F_4^+$(13.0), 69 CF_3^+(100), ^{19}F nmr: $\phi(CF_3)$ 80.8(t) [$J(CF_3-CF_2)$=13.5 Hz]; ϕ(CF) 186.1(mult). Found: C, 23.90%. Calculated for C_9F_{18}: C, 24.00%.

Perfluoro(1-cyclohexylpropane)(54) (nc) had bp 106.0～106.8 °C, n_D^{20}1.3096 abd d_4^{20}1.8216. IR: 1348 (m), 1319 (s), 1309 (m,sh), 1250 (vs), 1228 (s,sh), 1211 (vs), 1201 (s,sh), 1171 (m), 1158 (m,sh), 1141 (m), 1112 (w), 1066 (m), 1045 (w), 1025 (s), 1016 (m,sh), 988 (m), 955 (w,sh), 947 (m), 938 (m), 868 (w,sh), 853 (w), 842 (w), 817 (w), 784 (w), 745 (w), 715 (m), 705 (w), 665 (w), 618 (w), 586 (w), 530 (w). Mass: 381 $C_8F_{15}^+$(4.2), 281 $C_6F_{10}^+$(37.6), 243 $C_6F_9^+$(6.4), 231 $C_5F_9^+$(24.0), 193 $C_5F_7^+$(8.9), 181 $C_4F_7^+$(40.3), 169 $C_3F_7^+$(9.9), 162 $C_4F_6^+$(8.2), 143 $C_4F_5^+$(7.8), 131 $C_3F_5^+$(79.8), 119 $C_2F_5^+$(27.6), 100 $C_2F_4^+$(29.9), 93 $C_3F_3^+$(14.6), 69 CF_3^+(100), 31 CF^+(13.4). Found: C, 23.78%. Calculated for C_9F_{18}: C, 24.00%.

Perfluoro(3-methyl-1-oxaspiro[4.5]decane)(11b) (nc) had bp 127.2～127.5 °C, n_D^{20}1.3012 and d_4^{20}1.8655. IR: 1323 (vs), 1295 (vs), 1259 (vs), 1246 (s,sh), 1228 (ms,sh), 1201 (s), 1173 (w), 1125 (w), 1085 (w), 1058 (w), 1028 (s), 996 (m), 974 (s),

950 (w), 791 (m), 763 (w), 731 (ms), 638 (w), 615 (w), 573～588 (w), 508 (w). Mass: 459 $[M-F]^+$(88.0), 309 $C_7F_{11}O^+$(15.5), 293 $C_7F_{11}^+$(8.0), 281 $C_6F_{11}^+$(6.2), 243 $C_6F_9^+$(10.1), 219 $C_4F_9^+$(10.9), 200 $C_4F_8^+$(16.9), 181 $C_4F_7^+$(26.1), 169 $C_3F_7^+$(9.8), 150 $C_3F_6^+$(17.0), 131 $C_3F_5^+$(100), 119 $C_2F_5^+$(10.0), 93 $C_3F_3^+$(13.0), 69 CF_3^+(94.2), 31 CF^+(6.0). ^{19}F nmr: $\phi(\alpha\ CF_2)$ 75.5 and 82.1 (J_{AB}=138 Hz]; $\phi(CF_3)$ 73.5(mult); ϕ(CF) 181.9(mult). Found: C, 25.13%. Calculated for $C_{10}F_{18}O$: C, 25.11%.

Perfluoro(2-cyclohexylmethylpropionyl fluoride)(55)(nc) had bp 135.5～135.7 °C, n_D^{20}1.3052 and d_4^{20}1.8796. IR: 1891 and 1874 ν(c=o)(m), 1316 (ms), 1293 (s), 1238～1256 (s～vs), 1199 (s), 1176 (m), 1146 (m), 1111 (m), 1029 (ms), 1006 (w), 986 (w), 975 (ms), 931 (w), 786 (w), 748 (w), 736 (m), 636 (w). Mass: 459 $[M-F]^+$(3.8), 431 $C_9F_{17}^+$(2.3), 331 $C_7F_{13}^+$(2.6), 293 $C_7F_{11}^+$(3.4), 281 $C_6F_{11}^+$(5.6), 243 $C_6F_9^+$(5.6), 231 $C_5F_9^+$(4.8), 197 $C_4F_8O^+$(5.7), 181 $C_4F_7^+$(13.9), 169 $C_3F_7^+$(11.3), 150 $C_3F_6^+$(8.4), 131 $C_3F_5^+$(36.8), 119 $C_2F_5^+$(8.8), 100 $C_2F_4^+$(12.0), 69 CF_3^+(100), 47 COF^+(8.8), 31 CF^+(4.3). ^{19}F nmr: ϕ(-C(O)F) -32.2(mult); $\phi(CF_3)$ 72.1(mult); ϕ(CF-CF_3) 181.5(mult); ϕ(CF) 180.5(mult). Found: C, 24.98%. Calculated for $C_{10}F_{18}O$: C, 25.11%.

^{19}F nmr data of 54 are shown in Table 1.

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