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THE REACTION OF PERFLUOROBICYCLIC ETHERS AND PERFLUOROSPIRO-ETHERS WITH ANHYDROUS ALUMINUM CHLORIDE

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SUMMARY

Perfluorobicyclic ethers and perfluorospiroethers, all containing an oxolane skeleton, were treated with $AlCl_3$ in a heterogeneous manner to give the corresponding α,α,α′-trichlorinated and α,α-dichlorinated products, respectively. From perfluoroacetal compounds, for example, perfluoro(8-methoxy-7-oxabicyclo-[4.3.0]nonane), mono- and di-chlorinated products, i.e. perfluoro-(8-chloro-8-methoxy-7-oxabicyclo[4.3.0]nonane) and perfluoro-(8,8-dichloro-7-oxabicyclo[4.3.0]nonane) were obtained in good yields. The action of fuming sulfuric acid on these polychlorinated products led to the formation of the corresponding lactones. Perfluoro(6-chloro-7-oxa-8-oxobicyclo[4.3.0]nonane) was treated with $(CH_3)_2NLi$ to give N,N-dimethylundecafluoro-2-oxocyclohexylacetamide.

INTRODUCTION

In earlier papers, we have shown that perfluorobicyclic- and perfluorospiro-ethers can be obtained by the electrochemical fluorination of cycloalkyl-substituted carboxylic acids [1,2]. The reactions of these ethers with anhydrous $AlCl_3$ are now examined.

Five- and six-membered perfluorocyclic ethers, with or without perfluoroalkyl group(s) at the carbon α to oxygen, have been treated with $AlCl_3$ to give chloropolyfluoro-compounds by several workers. Interaction with $AlCl_3$ involves the substitution of chlorine for fluorines at the carbon α to oxygen and the breakdown of a C-O bond, viz.

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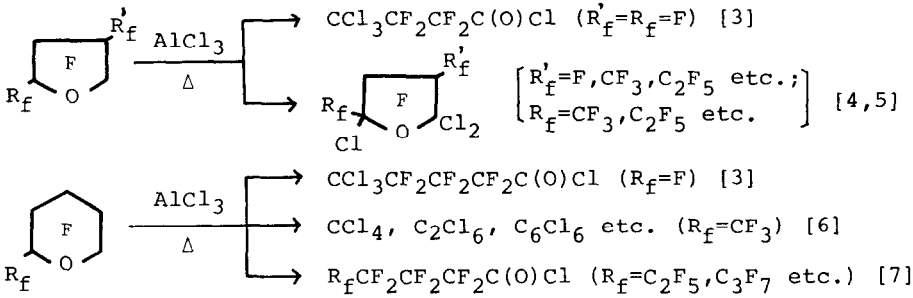
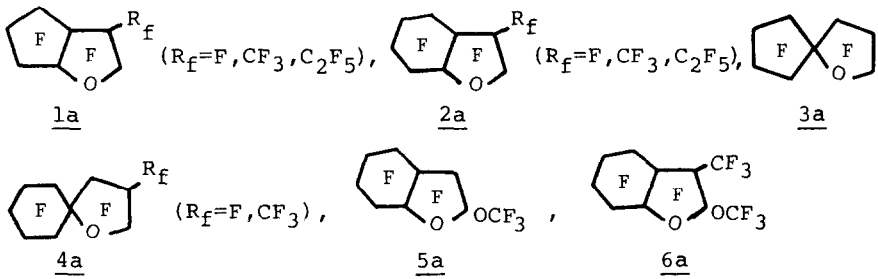


Scheme 1

Chlorination products with retention of skeleton were obtained only in the cases of perfluoro-oxolanes having an alkyl group at the α-carbon. However, no report has appeared on the reaction with perfluorobicyclic- and perfluorospiro-ethers except that of perfluoro(9-ethyl-8-methoxy-7-oxabicyclo[4.3.0]nonane)[2].

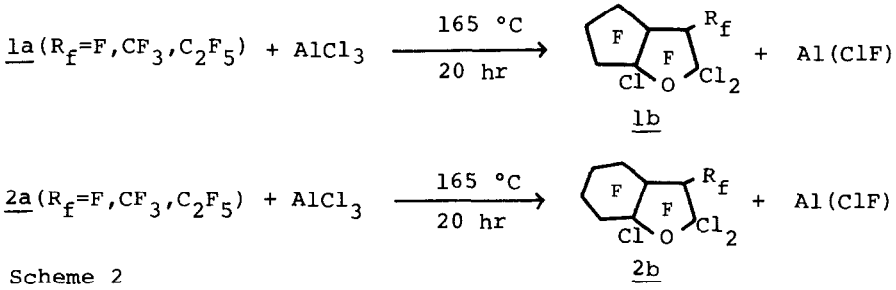
The perfluorocyclic ethers used in this investigation were perfluoro(4-alkyl-2-oxabicyclo[3.3.0]octane)s(1a), perfluoro-(9-alkyl-7-oxabicyclo[4.3.0]nonane)s(2a), perfluoro(1-oxaspiro-[4.4]nonane)(3a), perfluoro(3-alkyl-1-oxaspiro[4.5]decane)s(4a), perfluoro(8-methoxy-7-oxabicyclo[4.3.0]nonane)(5a) and perfluoro-(9-methyl-8-methoxy-7-oxabicyclo[4.3.0]nonane)(6a).



In this paper, we wish to report on the reaction of these perfluorobicyclic- and perfluorospiro-ethers with $AlCl_3$, some hydrolytic reactions of α,α,α'-trichlorinated and α,α-dichlorinated products with fuming H_2SO_4 to give the corresponding lactones, and also the reaction of perfluoro(6-chloro-7-oxa-8-oxobicyclo-[4.3.0]nonane)(2c) with $(CH_3)_2NLi$ as a nucleophile.

RESULTS AND DISCUSSION

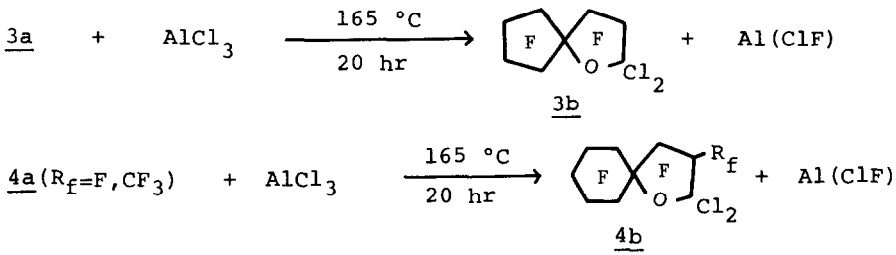
It has been shown that among several parameters the reaction temperature has most influence on the yield and purity of the chlorinated products in the reaction of perfluoroethers with $AlCl_3$ [5]. Furthermore, a higher reaction temperature within a range of 143~170 °C was needed to optimise the yields of the desired chlorinated products as the perfluoroalkyl group(s) attached to the 2- and 4-position of the oxolane ring became larger. On the premise that perfluorobicyclic ethers would react analogously, 2a(R_f=F) was treated at a reaction temperature of 165 °C for 20 hrs, and the trichlorinated product, 2b(R_f=F), was obtained in a yield of 71.8%. The selected conditions seemed to be appropriate, because a lower (143 °C) or a higher reaction temperature (180 °C) resulted in decreasing the yields of 2b(R_f=F) [Table 1]. So, for all other perfluorobicyclic- and perfluorospiro-ethers, the same reaction conditions as those for 2a(R_f=F) were applied [Table 2].



Scheme 2

In the reaction with 1a and 2a, a general trend was observed between the structure and the yields of chlorinated products: as R_f became larger (R_f=F→CF_3→C_2F_5), the yields of 1b and 2b decreased.

Similarly, spiroethers (3a and 4a) reacted and gave the corresponding dichlorinated products.



Scheme 3

TABLE 1

Reactions of 2a(R_f=F) with $AlCl_3$ at various temperature

Reactant (mmol)	Temp (°C) hr	Product[a] (Yield%)	Ether[b] (mmol)	Others (g)
Ether (7.4) $AlCl_3$ (15)	145/20	trace	6.9	$COCl_2$, CCl_4(trace)
Ether (7.4) $AlCl_3$ (15)	165/20	71.7	0.6	$COCl_2$, CCl_4, C_2Cl_6, C_6Cl_6(0.2)
Ether (7.5) $AlCl_3$ (15)	180/18	21.5	0.3	$COCl_2$, CCl_4, C_6Cl_6(0.5)

[a] 2b(R_f=F). Yields were calculated based on sample consumed.

[b] 2a(R_f=F) recovered.

TABLE 2

Summary of reactions of 1a, 2a, 3a, 4a, 5a and 6a with $AlCl_3$

Sample (A) (mmol)	Product (B) (Yield %)	Sample (A) Recovered (%)
1a(R_f=F) (5.42)[a]	1b(R_f=F) (63.3)	3.7
1a(R_f=CF_3) (7.16)[a]	1b(R_f=CF_3) (48.1)	15.3
1a(R_f=C_2F_5) (3.96)[a]	1b(R_f=C_2F_5) (55.4)	12.5
2a(R_f=F) (7.36)[a,b]	2b(R_f=F) (71.1)	8.1
2a(R_f=CF_3) (6.70)[a]	2b(R_f=CF_3) (49.0)	35.8
2a(R_f=C_2F_5) (6.43)[a]	2b(R_f=C_2F_5) (39.2)	21.9
3a (4.75)[a]	3b (84.0)	6.3
4a(R_f=F) (6.60)[a]	4b(R_f=F) (35.7)	2.4
4a(R_f=CF_3) (3.97)[a]	4b(R_f=CF_3) (27.8)	9.2
5a (3.72)[c]	7 (17.1), 8 (39.7), 2b(R_f=F) (trace)	32.1
6a (7.49)[c]	9 (16.0), 10 (21.2), 2b(R_f=CF_3) (trace)	14.9
6a (5.67)[a]	9 (trace), 10 (12.7), 2b(R_f=CF_3) (22.2)	0

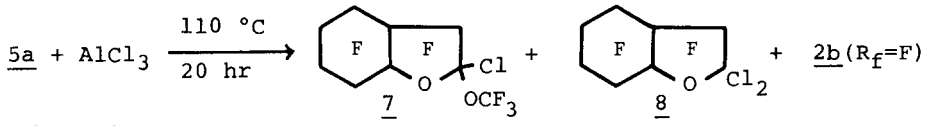
[a] Ethers were treated with 2 molar excess of $AlCl_3$ at 165 °C for 20 hrs.

[b] This datum is duplicated with that given in TABLE 1.

[c] About 1.5 molar excess of $AlCl_3$ was used and the reaction was conducted at 110 °C for 20 hrs.

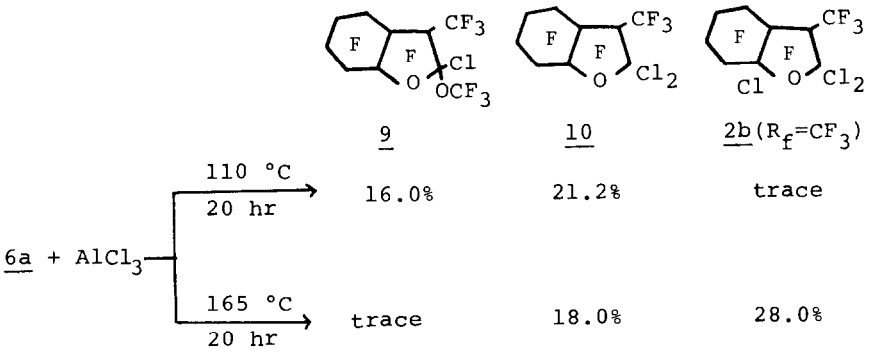
The formation of these trichlorinated (1b and 2b) and dichlorinated products (3b and 4b) from perfluorobicyclic- and perfluorospiro-ethers respectively provided additional evidence for the establishment of bicyclic- and spiro-ether linkages in the cyclization products from the fluorination of cycloalkyl-substituted carboxylic acids [1,2].

When perfluorobicyclic ethers having an acetal linkage like 5a and 6a were treated with $AlCl_3$, several kinds of chlorination products were formed. Thus, when 5a was treated with $AlCl_3$ at a moderate temperature (110 °C), perfluoro(8-chloro-8-methoxy-7-oxabicyclo[4.3.0]nonane)(7) and perfluoro(8,8-dichloro-7-oxabicyclo[4.3.0]nonane)(8), in both of which the α-fluorine at the ring juncture was left unaffected, were obtained in yields of 17.1% and 39.7%, respectively. Small quantities of perfluoro-(7,8,8-trichloro-7-oxabicyclo[4.3.0]nonane)[2b(R_f=F)] were also formed. When the reaction was started from 2a(R_f=F), even if carried out with use of a high molar ratio [2a(R_f=F) : $AlCl_3$ = 1 : 0.5] under moderate conditions, the products formed were always 2b(R_f=F) other than unreacted 2a(R_f=F), $COCl_2$, CCl_4 and C_2Cl_6.



Scheme 4

Similarly, 6a afforded perfluoro(9-methyl-8-chloro-8-methoxy-7-oxabicyclo[4.3.0]nonane)(9) and perfluoro(9-methyl-8,8-dichloro-7-oxabicyclo[4.3.0]nonane)(10) in yields of 16.0% and 21.2%, respectively, with a trace of 2b(R_f=CF_3) being formed. In these reactions, the degree of chlorination attained appeared to be largely a function of temperature, because, under analogous conditions but at a slightly higher reaction temperature (165 °C), the main products obtained were dichlor- and trichlorinated ones, viz:



Scheme 5

Though the α-fluorine at an acetal linkage of 5a and 6a showed facile reactivity toward $AlCl_3$, several attempted reactions with $AlBr_3$ and with strong nucleophiles such as CH_3ONa and $(CF_3)_2C{=}NLi$ failed to replace this α-fluorine.

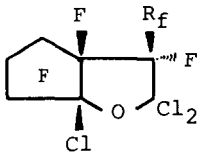
Since the energy difference between cis and trans forms are small for 5-6 and 6-6 fused-ring systems, perfluorobicyclic compounds are considered to be mixtures having both cis and trans fusions at the ring junctures [8].

On the other hand, halogens at the ring junctures of 1a and 1b are considered to be cis. The fact that the ^{19}F nmr spectra of both 1a(R_f=F) and 1b(R_f=F) are rather simple suggests that these are stereochemically pure and are assumed to be cis.

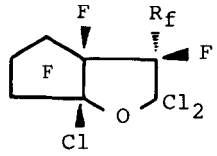
Recently, Tatlow and his co-workers investigated the fluorination of cyclooctane by the CoF_3 method, and found that not only perfluorocyclooctane and 1-H-pentadecafluorocyclooctane, but also cis-perfluorobicyclo[3.3.0]octane, were formed in appreciable yields [9]. The cis-structure of the last compound was confirmed by comparison with an authentic specimen which was prepared by the fluorination of the corresponding cis-bicyclo[3.3.0]octane. The lack of the trans is explained by the prohibitive strain of the 5-5 fused-ring system.

In the case of 1a and 1b carrying an alkyl group (R_f=CF_3 and C_2F_5) on the 4-position of the 5-5 fused ring, the existence of two isomers is possible depending on the direction of attachment toward the two halogens at the ring juncture which are cis.

For example, for 1b:



A form

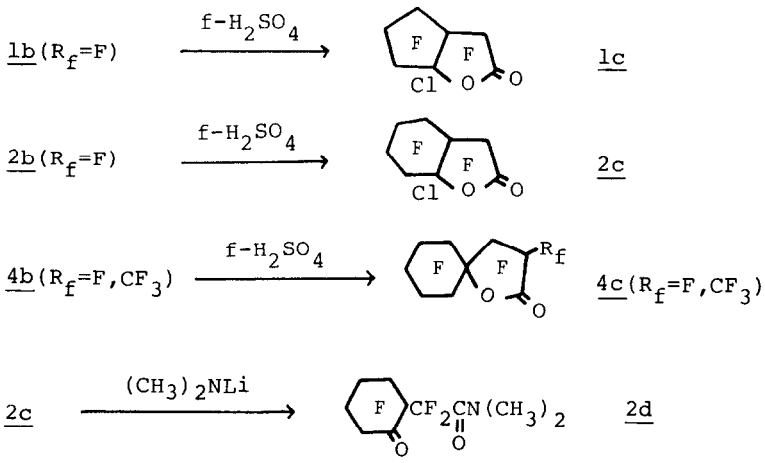


B form

Although the ^{19}F nmr spectra of 1a(R_f=CF_3,C_2F_5) did not exhibit much difference in chemical shifts between the two isomers, those of 1b(R_f=CF_3,C_2F_5) showed interesting conformational information. For example, in the spectrum of 1b(R_f=CF_3) [Fig. 1], two sets of absorption peaks appeared due to the CF_3 group at ϕ71.1 and ϕ72.4 ppm and the CF group at the 5-position at ϕ168.3 and ϕ169.6 ppm, in a ratio of 1 : 1.4, respectively. The peaks at ϕ143.3 and ϕ158.1 ppm, of which the absorption ratio was 1.4 : 1, were assigned to the CF group at the 4-position. The former one, which is more intense than the latter, was determined to be the one which was cis to the chlorine at the 1-position [B-form]. This assignment was based on our previous finding that the absorption peak due to the fluorine, which is located on the same side as the chlorine atom at the diagonal position of the furan ring, appears at lower field than that of the fluorine at the opposite site [5]. Furthermore, it was found that the configuration was predominantly the B-form when R_f=C_2F_5 by studying the spectrum of 1b(R_f=C_2F_5). Because an alkyl group present at a less crowded site would be more stable thermodynamically, the adoption of the B-form will be taken for granted.

Some chlorinated products were converted into perfluorolactones by treatment with fuming H_2SO_4. The synthetic potential of these lactones, involving a nucleophilic reaction of perfluoro(6-chloro-7-oxa-8-oxobicyclo[4.3.0]nonane)(2c) with $(CH_3)_2NLi$, is shown in Scheme 6.

From 1b(R_f=F), 2b(R_f=F), 4b(R_f=F) and 4b(R_f=CF_3), such lactones as 1c, 2c, 4c(R_f=F) and 4c(R_f=CF_3) were obtained in yields of 80.0%, 73.7%, 88.3% and 83.4%, respectively. These are fuming liquids in the air, and showed strong reactivity toward nucleophiles. Thus, with $(CH_3)_2NLi$, 2c gave N,N-dimethylundecafluoro-2-oxocyclohexylacetamide(2d) in a yield of 56.9%.



Scheme 6

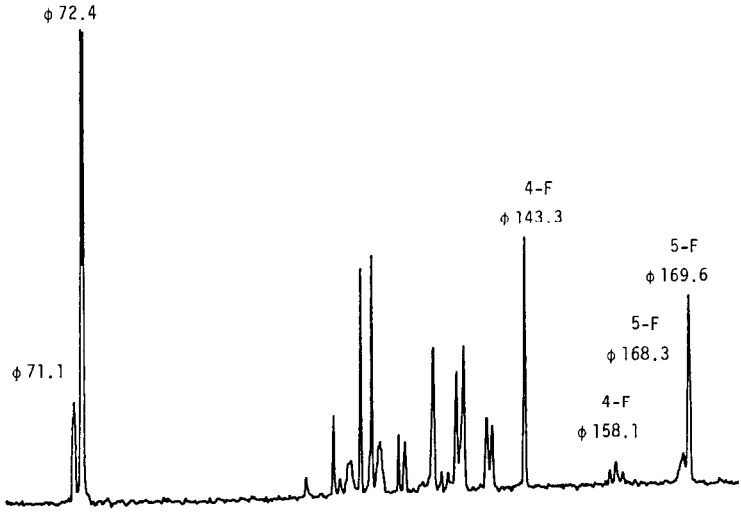


Fig. 1. ^{19}F nmr spectrum of 1b(R_f=CF_3)

EXPERIMENTAL

Starting materials and apparatus

The starting perfluorobicyclic- and perfluorospiro-ethers used were all made as previously described [1,2]. The other reagents were available commercially and used as received.

A Hoke bomb (capacity: 30 mℓ) with a stainless steel valve was used for the reaction of 1a-6a with $AlCl_3$, and a Pyrex vacuum line equipped with a Heise Bourdon tube gage was used for handling the volatile compounds.

^{19}F nmr spectra were recorded on a Hitachi R-20 spectrometer at 56.4 MHz using $CFCl_3$ as an internal reference (positive shifts are upfield from CCl_3F), while ^1H nmr spectra were 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 Shimadzu GCMS-7000 instrument.

Analytical work was carried out with a Shimadzu GC-1C gas chromatograph using a stainless steel column (3 mm dia) packed with 26% Kel F #90 on Chromosorb PAW (4.1 m). For semi-preparative work, a Shimadzu GC-1C gas chromatograph was used employing stainless steel columns (10 mm dia) packed with 30% Fluolube HG 1200 on Chromosorb PAW (4.1 m).

General procedure for the reaction of perfluorobicyclic ethers and perfluorospiroethers

To illustrate the general procedure for this reaciton, the respective reactions of 1a(R_f=C_2F_5)(as a typical example of the reaction of 1a and 2a), 3a (as a typical example of the reaction of 3a and 4a) and 5a (as a typical example of the reaction of 5a and 6a) will be described.

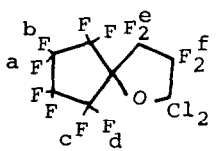
The reaction of 1a(R_f=C_2F_5)

In a 30 mℓ Hoke bomb, 1a(R_f=C_2F_5)(1.69 g, 3.96 mmoℓ) was condensed onto granular $AlCl_3$(1.1 g, 7.9 mmoℓ) and kept at 165 °C for 22 hrs. While the bomb was kept at 0 °C, 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 1a(R_f=C_2F_5), CCl_4 and a trace of 1b(R_f=C_2F_5) were found. The compounds which remained in the bomb were rinsed out several times with 5 mℓ of Daiflon S3 (1,1,2-trichlorotrifluoroethane) solvent. The solution was then removed from the green powder by filtration. After the major part of the solvent had been evaporated by use of a rotary evaporator, the liquid was analysed and purified. Thus, 1b(R_f=C_2F_5)(0.92 g, 55.4% Yield) was obtained. Small quantities

of C_2Cl_6 and C_6Cl_6 were also formed. Perfluoro(4-ethyl-1,3,3-trichloro-2-oxabicyclo[3.3.0]octane)[1b(R_f=C_2F_5)](nc) had bp 188.5~189.0 °C, n_D^{20}1.3750 and d_4^{20}1.8976. IR (capillary film): 1347 (s), 1333 (s), 1304 (s), 1273 (m), 1199~1232 (s), 1197 (s), 1146 (m,sh), 1141 (s), 1106 (s), 1083 (s), 1061 (m), 1042 (s), 1022 (s), 1109 (m,sh), 997 (m), 941 (m), 926 (m), 897 (s), 855 (m), 815 (m), 804 (m), 770 (s), 739 (s), 726 (s), 666 (w), 645 (m), 617 (m), 584 (w), 562 (w), 502 (w), 483 (w). Mass: 441 $[M-Cl]^+$(100), 259 $C_6F_8Cl^{35+}$(50.4), 209 $C_5F_6Cl^{35+}$(27.0), 119 $C_2F_5^+$(61.3), 109 $C_3F_2Cl^{35+}$(29.4), 100 $C_2F_4^+$(28.8), 85 CF_2Cl^{35+}(45.8), 69 CF_3^+(68.9), 63 $COCl^{35+}$(67.3). NMR: $\phi(CF_3)$ 80.5(mult); $\phi(CF\text{-}C_2F_5)$ 144.1(mult); $\phi(CF)$ 166.8(mult). Found: C, 22.58%. Calculated for $C_9F_{13}Cl_3O$: C, 22.62%.

The reaction of 3a with $AlCl_3$

Similarly, a reaction mixture of 3a(1.80 g, 4.75 mmol) and $AlCl_3$(1.3 g, 9.5 mmol) was kept in a Hoke bomb at 165 °C for 20 hrs. The work-up of the products was the same as that explained for the reaction of 1a(R_f=C_2F_5). Thus, 3b(1.53 g, 3.73 mmol) was obtained (Yield=84.0%). Perfluoro(3,3-dichloro-2-oxaspiro-[4.4]nonane)(3b)(nc) had bp 135.0~135.5 °C, n_D^{20}1.3483 and d_4^{20}1.8287. IR (capillary film): 1349 (m,sh), 1325 (s), 1310 (s), 1270 (s), 1249 (m,sh), 1211 (vs), 1194 (s,sh), 1166 (m), 1127 (w), 1084 (s), 1064 (m), 1049 (m), 1027 (m), 996 (s), 969 (s), 897 (s), 872 (s), 861 (m,sh), 781 (s), 670 (w), 651 (w), 612 (w), 592 (m), 566 (w), 551 (w), 539 (w). Mass: 391 $[M-F]^+$(5.5), $[M-Cl]^+$(39.9), 259 $C_6F_9O^+$(15.5), 243 $C_6F_9^+$(30.2), 181 $C_4F_7^+$(19.1), 131 $C_3F_5^+$(35.1), 119 $C_2F_5^+$(23.9), 109 $C_3F_3O^+$(13.7), 100 $C_2F_4^+$(22.0), 93 $C_3F_3^+$(13.4), 85 CF_2Cl^{35+}(28.8), 69 CF_3^+(100), 63 $COCl^{35+}$(35.9).



NMR: $\phi(CF^a)$ 124.8(mult), $\phi(CF^b)$ 130.6(mult) [J_{AB}=252 Hz]; $\phi(CF^c)$ 124.2(mult), $\phi(CF^d)$ 129.8 (mult)[J_{AB}=266 Hz]; $\phi(CF_2{}^e)$ 121.9(mult); $\phi(CF_2{}^f)$ 119.5(mult).

Found: C, 23.19%. Calculated for $C_8F_{12}Cl_2O$: C, 23.36%.

The reaction of 5a with $AlCl_3$

Similarly, a reaction mixture of 5a(1.65 g, 3.72 mmol) and $AlCl_3$(0.8 g, 6.0 mmol) was kept in a Hoke bomb at 110 °C for 20 hrs. Purification was initially conducted by trap-to-trap distillation using traps at -78 °C and -196 °C under dynamic pumping. The compounds at -196 °C were mostly HCl and $COCl_2$. Gas chromatographic separation of the products at -78 °C yielded the following compounds: 5a(0.53 g), 7(0.20 g, 17.1% yield), 8(0.71 g, 39.7% yield), 2b(R_f=F)(trace). Work-up of the residue in the bomb did not gave any additional amounts of chlorination products. Perfluoro(8-chloro-8-methoxy-7-oxabicyclo[4.3.0]nonane)(7)(nc) had bp 138.5~139.5 °C and n_D^{20}1.3249. IR(capillary film): 1325 (s), 1303 (m,sh), 1279 (vs), 1220~1250 (vs~s), 1172~1190 (vs), 1140 (vs), 1077 (s), 1059 (s), 1019 (vs), 997 (s), 965 (vs), 900 (ms), 890 (ms), 807 (s), 778 (m), 726 (w), 677 (m), 640 (ms), 629 (m), 602 (w), 542 (w), 509 (m). Mass: 425 $[M-Cl]^+$(8.5), 375 $[M-OCF_3]^+$(4.3), 321 $C_8F_{11}O^+$(3.1), 281 $C_6F_{11}^+$(3.6), 243 $C_6F_9^+$(9.9), 212 $C_5F_8^+$(18.3), 193 $C_5F_7^+$(5.4), 162 $C_4F_6^+$(5.2), 131 $C_3F_5^+$(13.8), 100 $C_2F_4^+$(4.4), 69 CF_3^+(100). NMR: $\phi(OCF_3)$ 54.7(mult); ϕ(CF) 189.6(mult). Found: C, 23.40%. Calculated for $C_9F_{15}O_2Cl$: C, 23.45%. Perfluoro(8,8-dichloro-7-oxabicyclo[4.3.0]nonane)(8)(nc) had bp 150.5~151.5 °C, n_D^{20}1.3551 and d_4^{20}1.8670. IR(capillary film): 1318 (s), 1298 (ms), 1247 (s,sh), 1235 (vs), 1223 (s,sh), 1215 (ms,sh), 1172 (vs), 1167 (ms,sh), 1136 (ms), 1110 (w), 1072~1082 (w), 1052~1060 (w), 1038 (m), 1017 (vs), 982 (s), 963 (vs), 924 (s), 872 (ms), 787 (s), 757 (w), 700 (w), 652 (ms), 644 (w), 627 (m), 602 (w), 514 (w). Mass: 375 $[M-Cl]^+$(100), 243 $C_6F_9^+$(47.6), 212 $C_5F_8^+$(89.5), 193 $C_5F_7^+$(28.8), 163 $C_3F_4OCl^{35+}$(18.3), 162 $C_4F_6^+$(25.8), 131 $C_3F_5^+$(40.6), 93 $C_3F_3^+$(20.0), 85 CF_2Cl^{35+}(22.2), 69 CF_3^+(31.0), 63 $COCl^{35+}$(20.5). NMR: ϕ(CF) 187.1(mult). Found: C, 23.31%. Calculated for $C_8F_{12}OCl_2$: C, 23.36%.

The other results of reactions including those of 1a(R_f=C_2F_5), 3a and 5a are summarized in Table 2 and the data characterising new chlorinated compounds are given below.

Perfluoro(1,3,3-trichloro-2-oxabicyclo[3.3.0]octane)[1b(R_f=F)](nc) had bp 153.0~153.5 °C, n_D^{20}1.3831 and d_4^{20}1.8426. IR(capillary film): 1350 (m), 1309 (s), 1287 (m,sh), 1265 (m), 1254 (m), 1210 (vs), 1165 (m), 1127 (w), 1078 (m), 1062 (m,sh),

1035 (s), 1015 (m), 999 (s), 949 (s), 926 (m), 884 (s), 875 (m,sh), 840 (m), 784 (s), 765 (w), 664 (w), 615 (w), 595 (w), 549 (w), 529 (w). Mass: 341 $[M-Cl]^+$(100), 278 $C_6F_9Cl^{35+}$(50.2), 228 $C_5F_7Cl^{35+}$(39.0), 209 $C_5F_6Cl^{35+}$(35.9), 131 $C_3F_5^+$(27.6), 85 CF_2Cl^{35+}(47.5), 69 CF_3^+(19.0), 63 $COCl^{35+}$(31.2). NMR: ϕ(CF) 171.0(mult). Found: C, 22.38%. Calculated for $C_7F_9Cl_3O$: C, 22.25%.

Perfluoro(4-methyl-1,3,3-trichloro-2-oxabicyclo[3.3.0]octane) [1b(R_f=CF_3)](nc) had bp 165.5~167.0 °C, n_D^{20}1.3773 and d_4^{20}1.8712. IR(capillary film): 1347 (s), 1301 (s), 1273 (m), 1252 (m,sh), 1226 (vs), 1199 (s), 1174 (w,sh), 1153 (m), 1134 (m), 1118 (w), 1087 (m,sh), 1080 (m), 1063 (w), 1045 (s), 1028 (s), 1010 (s), 973 (s), 912 (s), 875 (w), 857 (w), 826 (w), 775 (s), 732 (s), 665 (w), 639 (w), 616 (m), 591 (w). Mass: 391 $[M-Cl]^+$(100), 259 $C_6F_8Cl^{35+}$(54.7), 135 $C_2F_4Cl^{35+}$(51.8), 109 $C_3F_2Cl^{35+}$(29.2), 100 $C_2F_4^+$(29.8), 85 CF_2Cl^{35+}(42.6), 69 CF_3^+(65.0), 63 $COCl^{35+}$ (69.4). The ^{19}F nmr spectrum of 1b(R_f=CF_3) is shown in Fig. 1. Found: C, 22.48%. Calculated for $C_8F_{11}Cl_3O$: C, 22.46%.

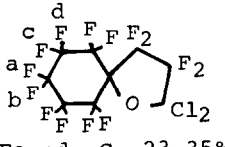
Perfluoro(6,8,8-trichloro-7-oxabicyclo[4.3.0]nonane)[2b(R_f= F)](nc) had bp 174.8~175.0 °C, n_D^{20}1.3833 and d_4^{20}1.8969. IR(capillary film): 1339 (m), 1330 (m), 1308 (m), 1286 (s), 1265 (m), 1251 (s,sh), 1233 (vs), 1198 (s,sh), 1186 (s), 1127 (m), 1091 (m), 1080 (m), 1047 (s), 1011 (s), 985 (s), 956 (m), 928 (s), 906 (m), 878 (s), 863 (w), 843 (w), 826 (w), 776 (s), 697 (w), 681 (w), 676 (w), 641 (m), 609 (w), 591 (w), 547 (w), 522 (w), 505 (w). Mass: 391 $[M-Cl]^+$(84.8), 259 $C_6F_8Cl^{35+}$(100), 132 $C_2F_3OCl^{35+}$(30.7), 131 $C_3F_5^+$(28.0), 93 $C_3F_3^+$(14.3), 85 CF_2Cl^{35+} (60.2), 74 $C_3F_2^+$(15.0), 69 CF_3^+(36.5), 63 $COCl^{35+}$(27.0). NMR: ϕ(CF) 170.9(mult). Found C, 22.47%. Calculated for $C_8F_{11}Cl_3O$: C, 22.46%.

Perfluoro(9-methyl-6,8,8-trichloro-7-oxabicyclo[4.3.0]- nonane)[2b(R_f=CF_3)](nc) had bp 191.5~192.5 °C, n_D^{20}1.3775 and d_4^{20}1.9218. IR (capillary film): 1350 (w,sh), 1331 (s), 1316 (s), 1295 (s), 1258 (s), 1237 (s), 1220 (vs), 1177 (s), 1153 (m), 1116 (s), 1084 (s), 1073 (m), 1049 (m), 1012 (s), 972 (s), 958 (s), 916 (s), 865 (w), 850 (s), 825 (m), 808 (s), 773 (s), 735 (s), 718 (w), 685 (w), 649 (m), 638 (m), 603 (w), 576 (w), 555 (w),

528 (w), 514 (m), 502 (m). Mass: 441 $[M-Cl]^+$(100), 309 $C_7F_{10}Cl^{35+}$(22.6), 259 $C_6F_8Cl^{35+}$(26.3), 182 $C_3F_5Cl^{35}O^+$(10.6), 135 $C_2F_4Cl^{35+}$(18.6), 131 $C_3F_5^+$(14.9), 100 $C_2F_4^+$(9.4), 85 CF_2Cl^{35+} (22.7), 69 CF_3^+(49.1), 63 $COCl^{35+}$(32.3). NMR: $\phi(CF_3)$ 70.5(mult); ϕ(CF) 169.5(mult). Found: C, 22.80%. Calculated for $C_9F_{13}Cl_3O$: C, 22.62%.

Perfluoro(9-ethyl-6,8,8-trichloro-7-oxabicyclo[4.3.0]nonane)[2b($R_f=C_2F_5$)](nc) had bp 204.5~205.5 °C, n_D^{20}1.3767 and d_4^{20}1.9456. IR (capillary film): 1380 (s), 1366 (m), 1205~2143 (vs), 1172 (s), 1144 (m), 1127 (s), 1099 (s), 1081 (s), 1046 (s,sh), 1034 (s), 1007 (s), 994 (s), 988 (s), 979 (s), 972 (s), 934 (m), 913 (s), 864 (m), 846 (s), 837 (w), 820 (w,sh), 805 (m), 800 (m), 768 (s), 741 (s), 731 (s), 722 (m), 688 (w), 668 (w), 653 (w), 640 (m), 630 (m), 602 (w), 587 (w), 548 (w), 529 (w), 503 (m), 487 (w). Mass: 491 $[M-Cl]^+$(100), 309 $C_7F_{10}Cl^{35+}$(35.0), 259 $C_6F_8Cl^{35+}$(34.8), 185 $C_3F_6Cl^{35+}$(24.1), 147 $C_3F_4Cl^{35+}$(21.8), 131 $C_3F_5^+$(24.2), 119 $C_2F_5^+$(94.3), 85 CF_2Cl^{35+}(48.5), 69 CF_3^+ (82.6). NMR: $\phi(CF_3)$ 79.1(mult); ϕ(CF) 167.7(mult). Found: C, 22.69%. Calculated for $C_{10}F_{15}Cl_3O$: C, 22.75%.

Perfluoro(3,3-dichloro-2-oxaspiro[4.5]decane)[4b(R_f=F)] (nc) had bp 156.0~158.5 °C, n_D^{20}1.3493 and d_4^{20}1.8768. IR(capillary film): 1333 (s,sh), 1324 (s), 1312 (s), 1285 (s), 1250 (vs), 1228 (s), 1214 (s), 1194 (vs), 1160 (w), 1124 (w), 1083 (s), 1048 (s), 1029 (m), 1010 (w), 986 (s), 961 (s), 910 (w), 887 (s), 870 (s), 840 (w), 776 (s), 728 (w), 667 (w), 642 (w), 634 (m), 610 (m), 587 (w), 516 (w), 485 (w), 459 (w). Mass: 441 $[M-F]^+$(3.9), 425 $[M-Cl]^+$(100), 293 $C_7F_{11}^+$(46.5), 243 $C_6F_9^+$ (38.3), 193 $C_5F_7^+$(15.0), 181 $C_4F_7^+$(29.3), 135 $C_2F_4Cl^{35+}$(28.8), 132 $C_2F_3OCl^{35+}$(22.3), 131 $C_3F_5^+$(49.5), 119 $C_2F_5^+$(18.1), 100 $C_2F_4^+$ (18.1), 93 $C_3F_3^+$(17.1), 85 CF_2Cl^{35+}(28.5), 69 CF_3^+(70.3), 63 $COCl^{35+}$(52.8).



NMR: $\phi(CF^a)$ 123.6(mult), $\phi(CF^b)$ 142.4(mult) [J_{AB}=294 Hz]; $\phi(CF^c)$ 122.4(mult), $\phi(CF^d)$ 140.1 (mult)[J_{AB}=282 Hz].
Found: C, 23.35%. Calculated for $C_9F_{14}Cl_2O$: C, 23.43%.

Perfluoro(4-methyl-3,3-dichloro-2-oxaspiro[4.5]decane) [4b(R_f=CF_3)](nc) had bp 171~172 °C, n_D^{20}1.3518 and d_4^{20}1.9026. IR(capillary film): 1321 (s,sh), 1309 (s), 1277 (vs), 1249 (s), 1228 (s), 1207 (s), 1187 (vs), 1165 (s), 1156 (m,sh), 1116 (m), 1094 (s), 1051 (m), 1031 (s), 980 (s), 966 (vs), 939 (w), 912 (w), 883 (m), 867 (s), 838 (w), 766 (m), 730 (s), 698 (w), 666 (w), 641 (w), 632 (w), 616 (m), 581 (w), 519 (w), 508 (w), 484 (w), 464 (w). Mass: 491 $[M-F]^+$(6.7), 475 $[M-Cl]^+$(100), 437 $C_{10}F_{14}OCl^{35+}$(6.2), 387 $C_9F_{12}OCl^{35+}$(7.1), 343 $C_8F_{13}^+$(6.9), 309 $C_7F_{11}O^+$(10.4), 293 $C_7F_{11}^+$(20.0), 243 $C_6F_9^+$(19.8), 181 $C_4F_7^+$(13.6), 178 $C_4F_5Cl^{35+}$(12.2), 131 $C_3F_5^+$(25.3), 100 $C_2F_4^+$(11.1), 85 CF_2Cl^{35+}(18.7), 69 CF_3^+(52.3), 63 $COCl^{35+}$(24.0). NMR: $\phi(CF_3)$ 70.9(mult); ϕ(CF) 157.3(mult) and 158.6(mult). Found: C, 23.65%. Calculated for $C_{10}F_{16}Cl_2O$: C, 23.48%.

Perfluoro(8-chloro-8-methoxy-9-methyl-7-oxabicyclo[4.3.0]-nonane)(9)(nc) had bp 149.3~150.0 °C, n_D^{20}1.3245 and d_4^{20}1.8790. IR(capillary film): 1326 (ms,sh), 1311 (s), 1282 (s), 1230~1260 (vs~s), 1182~1195 (vs), 1163 (vs), 1149 (vs), 1080 (s), 1061 (m), 1044 (ms), 1017 (s), 980 (m,sh), 965 (s), 889 (w,sh), 878 (m), 851 (w), 800 (ms), 774 (w), 737 (ms), 677 (w), 642 (m), 630 (w), 507 (w). Mass: 475 $[M-Cl]^+$(18.7), 425 $[M-OCF_3]^+$(8.4), 362 $C_8F_{14}^+$(8.6), 331 $C_7F_{13}^+$(8.1), 243 $C_6F_9^+$(17.7), 193 $C_5F_7^+$(8.5), 181 $C_4F_7^+$(14.7), 131 $C_3F_5^+$(19.8), 119 $C_2F_5^+$(6.2), 100 $C_2F_4^+$(6.0), 85 CF_2Cl^{35+}(6.2), 69 CF_3^+(100), 63 $COCl^{35+}$(8.0). NMR: $\phi(OCF_3)$ 54.9(mult); $\phi(CF_3)$ 72.1(mult); ϕ(CF-CF_3) 153.5(mult); ϕ(CF) 184.6(mult). Found: C, 23.47%. Calculated for $C_{10}F_{17}O_2Cl$: C, 23.51%.

Perfluoro(8,8-dichloro-9-methyl-7-oxabicyclo[4.3.0]nonane) (10)(nc) had bp 165.0~165.5 °C, n_D^{20}1.3519 and d_4^{20}1.8993. IR(capillary film): 1303~1336 (s~ms), 1278 (s,sh), 1256 (s), 1201~1234 (s~vs), 1186 (vs), 1161 (s), 1152 (s), 1142 (s), 1108 (w), 1074 (w), 1045 (ms), 1012 (vs), 971 (ms,sh), 963 (vs), 951 (ms), 881 (w), 856 (m), 837 (m), 781 (s), 772 (m), 734 (s), 697 (m), 654 (s), 644 (m), 628 (m), 604 (w), 593 (w), 545 (w), 515 (m), 505 (m). Mass: 441 $[M-F]^+$(6.9), 425 $[M-Cl]^+$(100),

362 $C_6F_{10}^+$(27.5), 293 $C_7F_{11}^+$(12.4), 243 $C_6F_6^+$(43.8), 193 $C_5F_7^+$ (22.0), 131 $C_3F_5^+$(37.5), 85 CF_2Cl^{35+}(27.5). NMR: $\phi(CF_3)$ 71.8 (mult); ϕ(CF) 182.6(mult). Found: C, 22.50%. Calculated for $C_9F_{14}Cl_2O$: C, 23.43%.

The reaction of 1b(R_f=F) with fuming H_2SO_4

In a Pyrex ampule (1.3 X 14.0 cm), 1.42 g(3.76 mmol) of 1b(R_f=F), 5.1 g of fuming H_2SO_4(30%) and a trace of $HgSO_4$ were held at 145 °C for 24 hrs. 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 fumed in the air, was carefully separated from the lower one using a separating funnel. The liquid thus obtained (0.97 g) was assigned as pure 1c based on ^{19}F nmr, GC and infrared analysis. The yield of 1c was 80.0%.

Perfluoro(1-chloro-3-oxo-2-oxa-bicyclo[3.3.0]octane)(1c) (nc) had bp 103.8~104.2 °C, n_D^{20}1.3442 and d_4^{20}1.7768. IR(capillary film): 1874 ν(c=o)(vs), 1356 (m), 1330 (s), 1298 (m), 1284 (w), 1267 (m), 1231 (s), 1202 (vs), 1186 (vs), 1166 (s), 1136 (s), 1103 (m), 1066 (m), 1051 (s), 995 (vs), 867 (s), 852 (s), 840 (m), 742 (w), 724 (w), 651 (w), 622 (w), 593 (w), 557 (w), 534 (w), 493 (w). Mass: 287 $[M-Cl]^+$(2.4), 278 $[M-CO_2]^+$ (25.8), 243 $C_6F_9^+$(27.8), 231 $C_5F_9^+$(23.1), 228 $C_5F_7Cl^{35+}$(52.2), 209 $C_5F_6Cl^{35+}$(38.0), 197 $C_4F_7O^+$(16.6), 181 $C_4F_7^+$(21.7), 178 $C_4F_5Cl^{35+}$(19.4), 147 $C_3F_4Cl^{35+}$(19.3), 131 $C_3F_5^+$(100), 109 $C_3F_3O^+$ (16.8), 100 $C_2F_4^+$(27.6), 93 $C_3F_3^+$(19.6), 83 CF_2Cl^{35+}(13.5), 69 CF_3^+(21.5), 63 $COCl^{35+}$(39.9). NMR: ϕ(CF) 185.9(mult). Found: C, 25.90%. Calculated for $C_7F_9ClO_2$: C, 26.05%.

The reaction of 2b(R_f=F) with fuming H_2SO_4

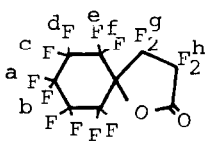
Similarly, a reaction mixture of 2b(R_f=F)(1.47 g, 3.45 mmol), fuming H_2SO_4(6.5 g) and a trace of $HgSO_4$ was kept in a Pyrex ampule at 145 °C for 24 hrs. The work-up of the product was the same as that explained for the reaction of 1b(R_f=F). Thus, 2c(1.00 g, 2.69 mmol) was obtained in a yield of 73.7%.

Perfluoro(6-chloro-8-oxo-7-oxabicyclo[4.3.0]nonane) (2c) (nc) had bp 123.0～123.5 °C, n_D^{20}1.3465 and d_4^{20}1.8330. IR(capillary film): 1876 ν(c=o)(vs), 1335 (s), 1322 (s), 1292 (m), 1271 (m), 1254 (s), 1220 (vs), 1197 (m,sh), 1176 (vs), 1156 (s), 1122 (s), 1099 (m), 1065 (s), 1043 (m), 986 (s), 914 (w), 880 (w,sh), 871 (w), 850 (m), 834 (m), 817 (s), 782 (w,sh), 752 (w), 725 (m), 672 (w), 655 (w), 628 (w), 622 (m), 603 (w), 592 (w), 569 (m), 511 (m), 462 (m). Mass: 337 $[M-Cl]^+$(4.4), 309 $C_7F_{11}O^+$(26.1), 281 $C_6F_{11}^+$(49.8), 259 $C_6F_8Cl^{35+}$(98.6), 243 $C_6F_9^+$ (22.2), 231 $C_5F_9^+$(24.5), 228 $C_5F_7Cl^{35+}$(35.0), 209 $C_5F_6Cl^{35+}$ (20.4), 181 $C_4F_7^+$(51.4), 178 $C_4F_5Cl^{35+}$(22.0), 131 $C_3F_5^+$(100), 109 $C_3F_2Cl^{35+}$(15.8), 100 $C_2F_4^+$(15.8), 93 $C_3F_3^+$(23.3), 85 CF_2Cl^{35+} (13.1), 69 CF_3^+(47.9), 63 $COCl^{35+}$(21.0). NMR: ϕ(CF) 184.9(mult). Found: C, 25.60%. Calculated for $C_8F_{11}ClO_2$: C, 25.77%.

The reaction of 3b(R_f=F) with fuming H_2SO_4

Similarly, a reaction mixture of 3b(R_f=F)(1.53 g,3.32 mmol), fuming H_2SO_4(4.5 g) and a trace of $HgSO_4$ was kept in a Pyrex ampule at 145 °C for 24 hrs. The work-up of the product was the same as that explained for the reaction of 1b(R_f=F). Thus, 3c(R_f=F)(1.19 g, 2.93 mmol) was obtained in a yield of 88.3%. It solidified at -78 °C.

Perfluoro(3-oxo-2-oxaspiro[4.5]decane)[3c(R_f=F)](nc) had bp 130.0～132.5 °C, n_D^{20}1.3206 and d_4^{20}1.8543. IR (capillary film): 1873 ν(c=o)(s), 1344 (m), 1311～1323 (m), 1286 (m), 1247 (s), 1192 (vs), 1170 (m,sh), 1123 (m), 1087 (m), 1058 (s), 1033 (w), 1025 (m), 976 (m), 961 (w), 916 (w), 885 (w,sh), 875 (w), 843 (w), 805 (m), 767 (w), 735 (w), 725 (w), 663 (w), 640 (w), 632 (m), 598 (w), 587 (w), 509 (w). Mass: 359 $[M-COF]^+$(3.5), 293 $C_7F_{11}^+$(38.7), 243 $C_6F_9^+$(57.2), 193 $C_5F_7^+$(27.0), 181 $C_4F_7^+$(29.1), 131 $C_3F_5^+$(100), 119 $C_2F_5^+$(21.1), 100 $C_2F_4^+$(37.3), 69 CF_3^+(44.0).



NMR: ϕ(CF^a) 126.7(mult), ϕ(CF^b) 139.5(mult) [J_{AB}=292 Hz]; ϕ(CF^c) 122.3(mult), ϕ(CF^d) 139.9 (mult)[J_{AB}=286 Hz]; ϕ(CF^e) 119.6(mult), ϕ(CF^f) 129.9(mult)[J_{AB}=293 Hz]; ϕ($CF_2{}^g$) 123.9 (mult); ϕ(CF_2) 119.5(mult). Found: C, 26.58%. Calculated for $C_9F_{14}O_2$: C, 26.60%.

The reaction of 3b(R_f=CF_3) with fuming H_2SO_4

Similarly, a reaction mixture of 3b(R_f=CF_3) (1.56 g, 3.35 mmol), fuming H_2SO_4 (6.5 g) and a trace of $HgSO_4$ was kept in a Pyrex ampule at 145 °C for 24 hrs. The work-up of the product was the same as that explained for the reaction of 1b(R_f=F). Thus, 3c(R_f=F) (1.16 g, 2.54 mmol) was obtained (Yield=83.4%).

Perfluoro(4-methyl-3-oxo-2-oxaspiro[4.5]decane) [3c(R_f=CF_3)] (nc) had bp 144.0~144.3 °C, n_D^{20}1.3284 and d_4^{20}1.8763.
IR(capillary film): 1863 ν(c=o)(s), 1832 (m), 1320 (s,sh), 1313 (s), 1283 (s), 1245 (vs,sh), 1225~1238 (vs), 1193 (vs), 1165 (m,sh), 1135 (m), 1104 (m), 1085 (m,sh), 1054 (w), 1024 (s), 990 (s), 967 (s), 945 (w), 928 (w,sh), 910 (w), 844 (w), 795 (m), 766 (w), 739 (w), 725 (w,sh), 705 (w), 670 (w), 632 (m), 602 (w), 485 (w). Mass: 437 $[M-F]^+$(1.6), 343 $C_8F_{13}^+$(9.0), 293 $C_7F_{11}^+$ (78.1), 259 $C_6F_9O^+$(19.6), 243 $C_6F_9^+$(69.9), 193 $C_5F_7^+$(14.2), 181 $C_4F_7^+$(22.3), 169 $C_3F_7^+$(12.6), 131 $C_3F_5^+$(100), 119 $C_2F_5^+$(12.2), 109 $C_3F_3O^+$(12.4), 100 $C_2F_4^+$(34.2), 93 $C_3F_3^+$(11.4), 69 CF_3^+(87.6). NMR: ϕ(CF_3) 75.2(mult); ϕ(CF) 177.3(mult). Found: C, 26.50%. Calculated for $C_{10}F_{16}O_2$: C, 26.32%.

The reaction of 2c(R_f=F) with $(CH_3)_2NLi$

2c(R_f=F) (1.85 g, 4.97 mmol) was condensed onto $(CH_3)_2NLi$ (5.5 mmol) in a 50 ml reaction vessel at -196 °C, and the solution was then warmed slowly to ambient temperature, After 18 hrs, the volatile product was separated by trap-to-trap distillation followed by GLC. Thus, N,N-dimethylundecafluoro-2-oxocyclohexylacetamide (2d) was obtained in a yield of 56.9%.

N,N-dimethylundecafluoro-2-oxocyclohexylacetamide (2d) (nc) had bp 156~157 °C and solidified at 34~37 °C.
IR (KBr pellet): 1655 (s,sh), 1643 (s), 1488 (w), 1442 (w), 1410 (m), 1442 (w,sh), 1324 (m), 1307 (m), 1290 (m), 1258 (m,sh), 1246 (m,sh), 1223 (s,sh), 1216 (s), 1189 (vs), 1177 (vs), 1158 (m,sh), 1146 (m,sh), 1122 (s), 1085 (m), 1061 (m), 1046 (m), 1002 (s), 956 (vs), 910 (m), 837 (m), 796 (m,sh), 791 (s), 716 (m), 686 (w,sh), 668 (m), 630 (m), 595 (w), 575 (w), 503 (m), 470 (w). Mass: 381 M^+(19.3), 362 $[M-F]^+$(11.3), 181 $C_4F_7^+$(18.6),

153 $C_5F_3ONH_3^+$(13.0), 131 $C_3F_5^+$(12.8), 72 $C(=O)C(CH_3)_2^+$(100), 69 CF_3^+(9.0). NMR: ϕ(CF) 177.9(mult); $\delta(CH_3)$ 3.23(s) and 3.00(s). Found: C, 31.61%. Calculated for $C_{10}F_{11}O_2NH_6$: C, 31.50%.

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