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Studies on the Reactions of Dichloro(perfluoroalkyl)amines with Protic Nucleophiles

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Dichloro(perfluoroalkyl)amines, R_fNCl_2, are reactive compounds whose synthesis is relatively straightforward. Exploitation of their chemistry occurs in their utilization as precursors to diazanes and, particularly, tetraazanes.[1−5] Also, metathetical replacement of the two chlorine atoms by other elements or groups provides a simple route to interesting compounds. The reaction of hydrochoric acid[5] or trimethylsilane[6] with CF_3NCl_2 gives CF_3NH_2. With phosphorus trichloride, $R_fCF_2NCl_2$ compounds are converted to the corresponding phosphazenes, $R_fCF_2N{=}PCl_3$ in high yields.[7] The chlorine atoms of R_fNCl_2 are displaced by selenium in reaction with $SeCl_2$ or Se to form $R_fN{=}SeCl_2$[8] or by sulfur in reaction with $SOCl_2$ to form $CF_3N{=}S{=}O$ or with $R_fN{=}SCl_2$ to give $R_fN{=}S{=}NR_f'$.[7,8]

The lability of fluorine bonded to the α-carbon in per or polyfluoroalkyl-containing nitrogen compounds is markedly enhanced. In fact, in some cases fluorine atoms in the α position are effective as fluorinating species.[9−11] Additionally, (perfluoroalkyl)amines eliminate HF readily to give nitriles via a carbimide intermediate.[5,6] Therefore, it is of interest to investigate the behavior of $R_fCF_2NCl_2$ toward protic nucleophiles.

Results and Discussion

The reactions of *N,N*-dichloro(pentafluoroethyl)amine (**1**) and *N,N*-dichloro(heptafluoropropyl)amine (**2**) with secondary amines in a 1:2 molar ratio in the presence of KF result in the formation of *N*-chloro(dialkylamino)(perfluoroalkyl)methanimines in 60% yield. The *N*-chloro(dialkyl)amines are also isolated and identified based on their spectral data (see Experimental Section). The same results are obtained in the absence of KF provided that more dialkylamine is added to absorb the HF formed during the reaction.

$$\underset{\mathbf{1,\,2}}{R_fCF_2NCl_2} + R_2NH \xrightarrow[-78\text{ to }25\,^\circ C,\ -HF]{KF} \underset{\mathbf{3-5}}{R_fC(NR_2){=}NCl} + R_2NCl + R_fCF{=}NCl \quad (1)$$

$R_f = CF_3$, **1**
$R_f = C_2F_5$, **2**
$R_f = CF_3$, $R = CH_3$, **3**
$R_f = C_2F_5$, $R = CH$, **4**
$R_f = C_2F_5$, $R = C_2H_5$, **5**

It is observed that the yields of **3−5** depend on the molar ratio of the reactants. Higher yields are obtained when more dialkylamine is used. Another example of such dependence is found when monochloramines $C_2F_5N(CF_3)Cl$ (**6**) and $C_3F_7N(CF_3)Cl$ (**7**), in which one chlorine atom of **1** and **2** is replaced by a trifluoromethyl group, are reacted with $(C_2H_5)_2NH$. If equimolar amounts of monochloroamine and dialkylamine are used, only the respective perfluoroazaalkenes and *N*-chlorodialkylamines are formed, *viz.*,

$$\underset{\mathbf{6,\,7}}{R_fCF_2N(CF_3)Cl} + (C_2H_5)_2NH \xrightarrow[-78\text{ to }25\,^\circ C,\ -HF]{KF} \underset{\mathbf{8,\,9}}{R_fCF{=}NCF_3} + \underset{\mathbf{10}}{(C_2H_5)_2NCl} \quad (2)$$

$R_f = CF_3$, **6**
$R_f = C_2F_5$, **7**
$R_f = CF_3$, **8**
$R_f = C_2F_5$, **9**

Compounds **8** and **9** are formed essentially quantitatively and are identified by comparison with literature ^{19}F NMR spectral data.[12,13] If excess of the dialkylamine is used, the corresponding (dimethylamino)(perfluoroalkyl)methanimine **11** is obtained.

$$\mathbf{7} + \underset{\text{excess}}{(CH_3)_2NH} \xrightarrow[-78\text{ to }25\,^\circ C,\ -HF]{KF} \underset{\mathbf{11}}{C_2F_5C[N(CH_3)_2]{=}NCF_3} + (CH_3)_2NCl \quad (3)$$

Compound **9**, obtained by another route, was shown to react easily with $(CH_3)_2NH$ to form **11**.

$$\mathbf{9} + (CH_3)_2NH \rightarrow \mathbf{11} \quad (4)$$

When isolated from the reaction mixture, $R_fCF{=}NCl$ does react with dialkylamine, albeit more slowly than does $R_fCF{=}NCF_3$.

From these results, we believe that the initial reaction in (1) could involve a species similar to **8** and **9** which would undergo further reaction with another molecule of amine to yield the product, *viz.*,

$$R_fCF_2NCl_2 + R_2NH \rightarrow [R_fCF_2NHCl] + R_2NCl$$

$$[R_fCF_2NHCl] \xrightarrow{-HF} R_fCF{=}NCl \xrightarrow{R_2NH} [R_fCF(NR_2)NHCl]$$

$$[R_fCF(NR_2)NHCl] \xrightarrow{-HF} R_fC(NR_2){=}NCl$$

The isolation of $R_fCF{=}NCl$ (identified by comparison with literature ^{19}F NMR data[14,15]) and the facile reaction of **9** with amine support this mechanism. It is obvious that the presence of the CF_3 group in **8** and **9** greatly increases their susceptibility

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to this nucleophilic attack. Failure of R_2NCl to react further with $R_fCF{=}NCF_3$ is additional evidence which supports the proposed mechanism. We have already seen that if a large excess of amine is used, monochloroamines **6** and **7** behave in the same manner as dichloroamines.

Similar results are obtained when methanethiol is used as a nucleophile in reaction with *N,N*-dichloro(perfluoroalkyl)amines **1** and **2**.

$$\mathbf{1} \text{ or } \mathbf{2} + CH_3SH \xrightarrow[-78 \text{ to } 25\ ^\circ C,\ -HF]{KF} \underset{\mathbf{12,\,13}}{R_fC(SCH_3){=}NCl} \qquad (5)$$

$$R_f = CF_3,\ \mathbf{12}$$
$$R_f = C_2F_5,\ \mathbf{13}$$

A notable fact is that both *N,N*-dichloro(perfluoroalkyl)amines and *N*-chlorobis(perfluoroalkyl)amines react with alcohols to give the same products. The ratio of the ester and orthoester products formed is a function of the amount of methanol utilized, while with ethanol, the formation of orthoester is essentially negligible, e.g.,

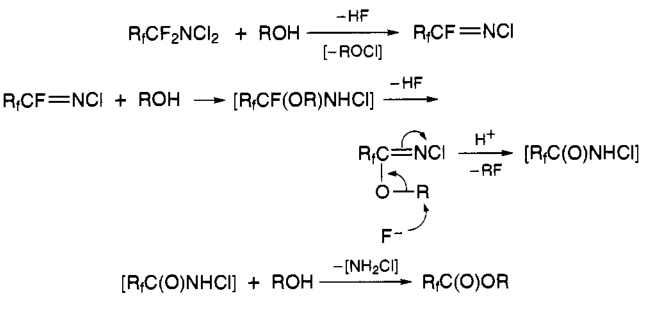
$$\underset{\substack{\mathbf{1,\,2}\\ \mathbf{14}\ (R_f = C_3F_7)}}{R_fCF_2NCl_2} + ROH \xrightarrow[-78 \text{ to } 25\ ^\circ C,\ -HF]{KF} \underset{\mathbf{15-19}}{R_fC(O)OR} + \underset{\mathbf{20-22}}{R_fC(OR)_3} \qquad (6)$$

$R_fC(O)OR$			$R_fC(OR)_3$		
R_f	R		R_f	R	
CF_3	C_2H_5	**15**	CF_3	CH_3	**20**
C_2F_5	CH_3	**16**	C_2F_5	CH_3	**21**
C_2F_5	C_2H_5	**17**	C_3F_7	CH_3	**22**
C_3F_7	CH_3	**18**			
C_3F_7	C_2H_5	**19**			

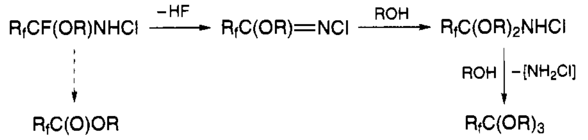
and

$$\underset{\mathbf{6}\text{ or }\mathbf{7}}{R_fCF_2N(CF_3)Cl} + C_2H_5OH \xrightarrow[-78 \text{ to } 25\ ^\circ C,\ -HF]{KF} \underset{\mathbf{15,\,17}}{R_fC(O)OR} \qquad (7)$$

Although at present we do not know the mechanistic detail with regard to the formation of these products, it could involve species similar to those mentioned above, e.g.,



The breaking of the carbon–oxygen bond in these cases is also suggested by Ishikawa.[9] For the formation of orthoesters, there are several aspects which should be taken into consideration in elucidating the reaction pathway. First, when $R_fC(O)OR$ is mixed with the alcohol under the same reaction conditions, no orthoester is detected. Second, the corresponding perfluoronitrile (R_fCN) does not give the ester or the orthoester with alcohols under similar reaction conditions. On the basis of these observations, we believe that the formation of the two products is a competitive process as outlined below.



It is obvious that the facile breakage of the O–R bond to form the carbonyl functionality in this case differentiates it from the reactions of amines and thiols with fluoroalkylamines.

Experimental Section

Materials. The starting materials $C_2F_5NCl_2$, $C_3F_7NCl_2$, $C_4F_9NCl_2$, $C_3F_7N(CF_3)Cl$, and $C_4F_9N(CF_3)Cl$, are prepared according to the literature methods.[16,17] Other chemicals were purchased as indicated: ClF (Ozark-Mahoning); CF_3CN, C_2F_5CN, C_3F_7CN (PCR); C_2H_5OH CH_3OH, $(CH_3)_2NH$, $(C_2H_5)_2NH$ (Aldrich).

General Procedures. A conventional Pyrex vacuum system equipped with a Heise Bourbon tube and Televac thermocouple gauges is used to handle gases and volatile liquids. Standard *PVT* techniques are employed to quantitate starting materials and volatile products. Trap-to-trap distillation and/or preparative gas chromatography (HP5710A) are used for purification. Infrared spectra are recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer with a 10-cm gas cell equipped with KBr windows. ^1H and ^{19}F NMR spectra are obtained with a Bruker AC 200 Fourier transform NMR spectrometer with $(CH_3)_4Si$ and $CFCl_3$ are references, and mass spectra are obtained with a VG 7070HS mass spectrometer. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

General Procedure for the Reaction of *N,N*-Dichloro(perfluoroalkyl)amines with Secondary Amines. A 100-mL glass reactor containing 12 mmol of sodium fluoride is evacuated at −196 °C, and 6 mmol of R_fNCl_2 and 12 mmol of dialkylamine are condensed into it. The mixture is warmed slowly from −78 to +25 °C with stirring. The products are fractionated by trap-to-trap distillation.

Properties of $CF_3C[N(CH_3)_2]{=}NCl$, (3). This compound is found as a colorless liquid in 60% yield in the trap at −20 °C ($C_2F_5NCl_2$ + $(CH_3)_2NH$). Spectral data are as follows. IR (film): 2940 m, 1616 s, 1560 m, 1575 s, 1457 s, 1382 s, 1275 s, 1228 s, 1185 s, 1097 s, 1066 m, 775 m cm^{-1}. ^{19}F NMR: δ −62.5 (CF_3, s). ^1H NMR: δ 3.0 (CH_3, s). MS (EI) [*m/e* (species) intensity]: 177/175 ($M^+ + 1$) 1/3, 142/140 ($M^+ - CH_3F$) 6/14.2, 139 ($M^+ - Cl$) 9, 110 ($M^+ - C_2H_6Cl + 1$) 16, 96 ($CF_3C{=}N^+ + 1$) 100, 69 (CF_3^+) 100. Anal. Calcd for $C_4H_6F_3ClN_2$: C, 27.58; H, 3.44; N, 16.09. Found: C, 27.64; H, 3.50; N, 16.07.

Properties of $C_2F_5C[N(CH_3)_2]{=}NCl$, (4). This compound is found as a colorless liquid in 60% yield in the trap at −20 °C ($C_3F_7NCl_2$ + $(CH_3)_2NH$). Spectral data are as follows. IR (film): 2840 w, 1621 s, 1481 m, 1442 m, 1372 s, 1336 s, 1235 s, 1166 vs, 1113 s, 1066 m, 1026 s, 884 s, 737 s cm^{-1}. ^{19}F NMR: δ −80.4 (CF_3, t), −109.6 (CF_2, q). ^1H NMR: δ 2.85 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 227/225 ($M^+ + 1$) 3.2/10.2, 226/224 (M^+) 0.7/2.1, 207/205 ($M^+ -$ HF) 1.6/3.9, 190 ($M^+ + 1 - Cl$) 12.7, 189 ($M^+ - Cl$) 17.1, 173/171 ($M^+ - CH_3F_2$) 1.8/5.5, 160 ($M^+ - C_2H_6Cl + 1$) 30.9, 146 ($CF_3CF_2C{=}N^+ + 1$) 100, 119 ($C_2F_5^+$) 71.5, 100 ($C_2F_4^+$) 4.4, 69 (CF_3^+) 100. Anal. Calcd for $C_5H_6F_5ClN_2$: C, 26.72; H, 2.67; N, 12.50. Found: C, 26.97; H, 2.80; N, 12.53.

Properties of $C_2F_5C[N(CH_3CH_2)_2]{=}NCl$, (5). This compound is found as a colorless liquid in 56% yield in the trap at −20 °C (C_3F_7-

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NCl_2 + $(CH_3CH_2)_2NH$). Spectral data are as follows. IR (film): 2983 m, 2942 m, 1608 s, 1451 m, 1386 m, 1382 m, 1277 m, 1231 s, 1178 vs, 1114 s, 1070 s, 1040 s, 984 m, 759 m, 736 s cm^{-1}. ^{19}F NMR: δ −80.7 (CF_3, t), −109.0 (CF_2, q). ^1H NMR: δ 3.36 (CH_2, q), 1.15 (CH_3, t). MS (CI^+) [*m/e* (species) intensity]: 255/253 ($M^+ + 1$) 10.5/33.0, 235/233 ($M^+ - F$) 7.0/18.6, 217 ($M^+ - Cl$) 63.0, 189 ($M^+ - C_2H_5Cl + 1$) 97.2, 146 ($CF_3CF_2C{=}N^+ + 1$) 34.1, 119 ($C_2F_5^+$) 16.0, 72 ($N[CH_3CH_2]_2^+$) 20.1, 69 (CF_3^+) 38.1, 56 ($N[CH_2CH_2]CH_2^+$) 100.

Properties of $(CH_3CH_2)_2NCl$, (10). This compound is found as a colorless liquid in 87% yield in the trap at −60 °C. After 2 weeks in a sealed tube, it turns black. Spectral data are as follows. IR (film): 2991 m, 2948 m, 1549 m, 1451 m, 1385 s, 1350 s, 1055 s, 736 s cm^{-1}. ^1H NMR: δ 2.95 (q, 2H, CH_2), 1.20 (t, 3H, CH_3). MS (EI^+) [*m/e* (species) intensity]: 109/107 (M^+) 11.3/33.8, 94/92 ($M^+ - CH_3$) 34.7/94.4, 80/78 ($M^+ - C_2H_5$) 3.5/10.2, 66/64 ($C_2H_5Cl^+$) 38.6/100.

Properties of $CF_3CF_2C[N(CH_3)_2]{=}NCF_3$, (11). This compound is found as a colorless liquid in 91% yield in the trap at −20 °C ($C_2F_5CF_2N(CF_3)Cl$ + $(CH_3)_2NH$). Spectral data are as follows. IR (film): 2963 w, 1678 m, 1650 m, 1285 s, 1252 m, 1212 s, 1174 s, 1112 s, 1035 s, 737 s cm^{-1}. ^1H NMR: δ 3.0 (CH_3). ^{19}F NMR: δ −45.5 (s, 3F, NCF_3), −80.5 (s, 3F, CF_2CF_3), −110.3 (s, 2F, CF_3CF_2). MS (CI^+) [*m/e* (species) intensity]: 259 ($M^+ + 1$) 79.4, 258 (M^+) 70.6, 243 ($M^+ - CH_3$) 77.6, 240 ($M^+ - F + 1$) 21.3, 239 ($M^+ - F$) 100, 189 ($M^+ - CF_3$) 15.2, 160 ($M^+ - CF_3NCH_3$) 10.7, 138 ($M^+ - C_2F_5$) 24.7, 119 ($C_2F_5^+$) 3.6, 69 (CF_3^+) 45.9.

The reaction of R_fNCl_2 with CH_3SH followed the same procedure as described above.

Properties of $CF_3C(SCH_3){=}NCl$ (12). This compound is found as a colorless liquid in 60% yield in the trap at −20 °C ($C_3F_7NCl_2$ + CH_3SH). Spectral data are as follows. IR (film): 2938 w, 1630 m, 1481 m, 1443 m, 1414 s, 1299 s, 1219 s, 1175 s, 984 m, 806 m, 727 m, 701 s cm^{-1}. ^{19}F NMR: δ −69.0 (CF_3, s). ^1H NMR: δ 2.88 (CH_3, s). ME (EI) [*m/e* (species) intensity]: 179/177 (M^+) 36/95, 160/158 ($M^+ - F$) 15/44.0, 142 ($M^+ - Cl$) 100, 81 (CF_3C^+) 3.8, 69 (CF_3^+) 37.0.

$C_2F_5C(SCH_3){=}NCl$ (13) stops as a colorless liquid in 70% yield in the trap at −20 °C ($C_3F_7NCl_2$ + CH_3SH). Spectral data are as follows. IR (film): 2934 w, 1603 m, 1480 m, 1334 s, 1203 s, 1135 m, 1070 m, 855 m, 734 s, 711 m cm^{-1}. ^{19}F NMR: δ −81.7 (CF_3, t), −112.5 (CF_2, q). ^1H NMR: δ 3.0 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 230/228 ($M^+ + 1$) 9/29, 229/227 (M^+) 40/100, 210/208 ($M^+ - F$) 14/39.0, 192 ($M^+ - Cl$) 100, 146 ($CF_3CF_2C{=}N^+ + 1$) 23.5, 119 ($C_2F_5^+$) 12.4, 69 (CF_3^+) 36.5. Anal. Calcd for $C_4H_3F_5ClNS$: C, 21.14; H, 1.32; N, 6.15. Found: C, 21.28; H, 1.42; N, 6.10.

General Procedure for the Reactions of *N,N*-Dichloro(perfluoroalkyl)amines with Alcohols. In a typical reaction, 5 mmol of R_fNCl_2 and an excess (15 mmol) of methanol (ethanol) are condensed at −196 °C into a 100-mL Pyrex round-bottomed flask (with or without NaF) fitted with a Teflon stopcock. The mixture is put into an −78 °C bath and is allowed to warm to 25 °C (about 12 h) with constant stirring. The products are separated by trap-to-trap distillation under vacuum. The contents of the traps at −20 or −60 °C are further purified by preparative GC.

Properties of $C_3F_7C(OCH_3)_3$. This compound is found as a colorless liquid in 42% yield in the trap at −20 °C ($C_4F_9NCl_2$ + CH_3OH). Spectral data are as follows. IR (film): 2997 m, 2861 s, 1451 m, 1344 m, 1283 s, 1226 s, 1166 vs, 1133 vs, 934 s, 735 m cm^{-1}. ^{19}F NMR: δ −81.2 (CF_3, t), −119.2 (CF_2CO, t), −126.5 (CF_3CF_2, tq). ^1H NMR: δ 3.44 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 255 ($M^+ - F$) 12.4, 243 ($M^+ - CH_3O$) 100, 181 ($C_4F_7^+$) 8.9, 169 ($C_3F_7^+$) 5.6, 119 ($C_2F_5^+$) 14.9, 69 (CF_3^+) 14.7, 59 ($C_2H_3O_2^+$) 15.9. Anal. Calcd for $C_7H_9F_7O_3$: C, 30.66; H, 3.28; F, 48.54. Found: C, 31.13; H, 3.24; F, 47.90.

Properties of $C_3F_7C(O)OCH_3$. This compound is found as a colorless liquid in 44% yield in the trap at −60 °C ($C_4F_9NCl_2$ + CH_3OH). Spectral data are as follows. IR (gas): 2973 w, 2933 w, 1800 s, 1447 m, 1359 m, 1309 s, 1273 s, 1236 vs, 1197 vs, 1146 s, 1090 s cm^{-1}. ^{19}F NMR: δ −81.7 (CF_3, t), −119.8 (CF_2CO, t), −127.5 (CF_3CF_2, tq). ^1H NMR: δ 3.96 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 229 ($M^+ + 1$) 12.4, 197 ($M^+ - CH_3O$) 2.2, 169 ($C_3F_7^+$) 31.5, 119 ($C_2F_5^+$) 25.1, 109 ($M^+ - C_2F_5$) 1.9, 100 ($C_2F_4^+$) 12.5, 69 (CF_3^+) 51.9, 59 ($M^+ - C_3F_7$) 95.6. Anal. Calcd for $C_5H_3F_7O_2$: C, 26.33; H, 1.33; F, 58.31. Found: C, 25.69; H, 1.28; F, 58.50.

Properties of $C_2F_5C(O)OCH_3$. This compound is found as a colorless liquid in 25% yield as a colorless liquid in the trap at −70 °C ($C_3F_7NCl_2$ + CH_3OH). Spectral data are as follows. IR (gas): 2970 w, 1801 s, 1447 m, 1313 s, 1232 vs, 1202 vs, 1160 vs, 1042 vs, 737 s cm^{-1}. ^{19}F NMR: δ −83.2 (CF_3, t), −121.8 (CF_2, t). ^1H NMR: δ 3.97 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 179 ($M^+ + 1$) 100, 159 ($M^+ - F$) 13.9, 147 ($M^+ - CH_3O$) 5.8, 119 ($C_2F_5^+$) 42.0, 69 (CF_3^+) 27.9, 59 ($M^+ - C_2F_5$) 88.7.

Properties of $C_2F_5C(OCH_3)_3$. This compound is found as a colorless liquid in 73% yield in the trap at −20 °C ($C_3F_7NCl_2$ + CH_3OH). Spectral data are as follows. IR (film): 2999 m, 2968 m, 2860 s, 1452 m, 1346 m, 1284 s, 1226 vs, 1167 vs, 1134 vs, 1062 vs, 1022 s, 934 s, 753 m, 736 m cm^{-1}. ^{19}F NMR: δ −81.7 (CF_3, t), −122.2 (CF_2, q). ^1H NMR: δ 3.43 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 205 ($M^+ - F$) 100, 143 ($C_4H_3F_4O^+$) 11.0, 119 ($C_2F_5^+$) 10.1, 69 (CF_3^+) 10.0. Anal. Calcd for $C_6H_9F_5O_3$: C, 32.15; H, 4.02; F, 42.38. Found: C, 32.25; H, 3.91; F, 42.40.

Properties of $CF_3C(O)OCH_2CH_3$. This compound was found in the trap at −70 °C ($C_2F_5NCl_2$ + CH_3CH_2OH). Spectral data are as follows. IR (gas): 2997 m, 1801 s, 1352 m, 1236 vs, 1202 vs, 1187 vs, 1152 vs, 1054 m, 1030 m, 736 s. ^{19}F NMR: δ −75.5 (CF_3, s). ^1H NMR: δ 4.25 (CH_2, q), 1.35 (CH_3, t). MS (EI) [*m/e* (species) intensity]: 141 ($M^+ - 1$) 14.9, 127 ($M^+ - CH_3$) 57.0, 113 ($M^+ - CH_2CH_3$) 22.7, 97 ($M^+ - C_2H_5O$) 47.1, 73 ($M^+ - CF_3$) 23.3, 69 (CF_3^+) 100.

Reactions of $C_3F_7N(CF_3)Cl$ and $C_4F_9N(CF_3)Cl$ with ethanol are conducted by using the same procedure as described above. The products obtained are identical to those obtained when $C_3F_7NCl_2$ and $C_4F_9NCl_2$ are reacted with ethanol. The spectral data of the products are as follows.

$CF_3CF_2C(O)OCH_2CH_3$. IR (gas): 1795 s, 1384 m, 1352 m, 1306 s, 1230 s, 1200 vs, 1157 vs, 1044 vs, 972 s, 736 s cm^{-1}. ^{19}F NMR: δ −82.9 (CF_3, t), −121.9 (CF_2, q). ^1H NMR: δ 4.42 (CH_2, q), 1.38 (CH_3, t). MS (EI) [*m/e* (species) intensity]: 191 ($M^+ - 1$) 2.0, 177 ($M^+ - CH_3$) 4.8, 163 ($M^+ - CH_2CH_3$) 3.3, 147 ($M^+ - C_2H_5O$) 22.8, 119 ($C_2F_5^+$) 100, 73 ($M^+ - C_2F_5$) 2.0, 69 (CF_3^+) 68.5. MS (CI^+) [*m/e* (species) intensity]: 193 ($M^+ + 1$) 12.2, 177 ($M^+ - CH_3$) 3.7, 173 ($M^+ - F$) 6.8, 163 ($M^+ - CH_2CH_3$) 7.3, 147 ($M^+ - C_2H_5O$) 19.6, 119 ($C_2F_5^+$) 100, 73 ($M^+ - C_2F_5$) 3.8, 69 (CF_3^+) 55.3. Anal. Calcd for $C_5H_5F_5O_2$: C, 31.26; H, 2.63. Found: C, 31.45; H, 2.65.

$CF_3CF_2CF_2C(O)OCH_2CH_3$. IR (gas): 2956 w, 2820 w, 1796 s, 1380 m, 1307 m, 1272 s, 1244 vs, 1197 s, 1150 vs, 1088 vs, 1048 s, 970 s, 737 s cm^{-1}. ^{19}F NMR: δ −81.1 (CF_3, t), −119.7 (CF_2CO, t), −127.3 (CF_3CF_2, tq). ^1H NMR: δ 4.42 (CH_2, q), 1.37 (CH_3, t). MS (EI) [*m/e* (species) intensity]: 241 ($M^+ - 1$) 1.9, 227 ($M^+ - CH_3$) 2.8, 213 ($M^+ - CH_2CH_3$) 4.5, 197 ($M^+ - C_2H_5O$) 18.1, 169 ($C_3F_7^+$) 100, 119 ($C_2F_5^+$) 25.9, 73 ($M^+ - C_3F_7$) 0.6, 69 (CF_3^+) 91.9. Anal. Calcd for $C_6H_5F_7O_2$: C, 29.76; H, 2.09; F, 54.94. Found: C, 29.59; H, 2.09; F, 54.50.

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