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SYNTHESIS OF FLUORINATED TERTIARY DIAMINES AND DIAZANES *

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SUMMARY

A variety of fluorinated and partially fluorinated tertiary diamines and diazanes have been prepared from 1-[bis(trifluoromethyl)amino]tetrafluoro-2-azapropene, which is obtained from the dimerization of 2-azapropene in the presence of CsF. Addition of ClF results in the formation of the tertiary diamine $(CF_3)_2NCF_2N(Cl)CF_3$. Insertion of alkenes and nitriles into the nitrogen-chlorine bond, as well as photolytic reactions with SF_5Cl and $CF_3C(O)Cl$, occurs readily. Attempts to prepare diazanes that contain polyfluoroalkyl groups from polyfluoroalkoxy imines, e.g., $R_fN{=}C(OR_f')_2$ ($R_f = CF_3$, SF_5; $R_f' = CH_2CF_3$, $CH(CF_3)_2$) resulted in breaking of the carbon-nitrogen double bond on reaction of the imine with ClF to give R_fNCl_2 and $F_2C(OR_f')_2$. Similarly $(CF_3)_2NC(OCH_2CF_3){=}NCF_3$ with ClF gives CF_3NCl_2 and $(CF_3)_2NCF_2OCH_2CF_3$.

INTRODUCTION

While the potential uses for fluorinated tertiary amines and diamines, as well as diazanes, are quite broad, e.g., as refrigerants, flame retardant coatings, hydraulic fluids, heat transfer media, turbine impellants, dielectrics [1], lubricants [2], fuel additives, blood substitutes [3] and as curing agents for fluoroepoxy resins [4], the single predominant method of preparation is electrochemical fluorination [1]. The products obtained by this method are generally isomeric mixtures of poly- and perfluorinated amines or diamines. They are difficult to purify and are obtained in yields ranging from 5 to 50%. Thus the use of these materials has been hampered and much of the data reported in the literature is suspect [1] because of impurities present in the samples originally studied. Other methods for the preparation of fluorinated tertiary amines, and diamines include: irradiation of a mixture of $(CF_3)_2NOCF_3$ and $CF_3N{=}CF_2$ to give a 10% yield of

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$(CF_3)_2NCF_2N(CF_3)OCF_3$ [5]; when perfluorocyclobutene is passed through a solution of $(CF_3)_2NCs$ in diglyme, an 82% yield of the cyclo-1-butenediamine is obtained [6]; photolysis of $[(CF_3)_2N]_2Hg$ and perfluorocyclobutene results in a 25% yield of the cyclobutanediamine [5]; refluxing $(CF_3)_2NCBr-CHN(CF_3)_2$ with KOH gives $(CF_3)_2NC=CN(CF_3)_2$ in 97% yield [7], while $(CF_3)_2NCHFCFBrN(CF_3)_2$ and KOH form $(CF_3)_2NCF-CFN(CF_3)_2$ at 20 °C in vacuum [8]; $(CF_3)_2NBr$ reacts with C_2F_4 at room temperature in daylight to give good yields of $(CF_3)_2NC_2F_4Br$ [9]; photolysis of $(CF_3)_2CFNClC_2F_5$ produces $C_2F_5(CF_3)NCF(CF_3)_2$ [10]; $(CHF_2)_3N$ is obtained from the fluorination of $(CHCl_2)_3N$ with antimony pentafluoride [11], and other partially fluorinated tertiary amines have resulted from the fluorination of secondary amides with SF_4 in the presence of KF [12]. A variety of tertiary amines that contain the SF_5 functional group have also been prepared from the mercurial $Hg[N(CF_3)SF_5]_2$, [13] as well as by other methods [14]. In addition, we have recently described a simple method for the preparation of poly-fluoroalkyltertiary amines from N,N-dichloroperfluoroalkyl amines [15]. In this paper, we report on the extension of this method to the preparation of a series of per- and polyfluoroalkyl diamines and diazanes.

RESULTS AND DISCUSSION

Perfluoroazaalkenes are easily prepared from appropriately substituted N-chloroamines [15,16], for example

$$CF_3N(Cl)CF_2CFCl_2 \xrightarrow{h\nu} CF_3N-CF_2 + CFCl_3$$

It is also well known that perfluoroazapropene dimerizes in the presence of CsF as shown [17].

$$CF_3N-CF_2 \xrightarrow{CsF} (CF_3)_2NCF-NCF_3$$

1

We have taken advantage of these two reactions to prepare a variety of fluorinated alkyldiamines and azanes.

Reaction of 1 with chlorine monofluoride at -78 °C resulted in a 75% yield of $(CF_3)_2NCF_2N(Cl)CF_3$ 2. This new N-chlorodiamine then undergoes reaction chemistry typical of secondary N-haloamines [9]. Photolysis in the absence of other reactants provides a 80% yield of diazane $[(CF_3)_2NCF_2(CF_3)N]_2$ 3. In mixtures with fluorinated alkenes or nitriles, insertion into the nitrogen-chlorine bond is readily achieved

$$2 + CF_2{=}CFCl \xrightarrow[5\text{-}7\ h]{h\nu} (CF_3)_2NCF_2N(CF_2CFCl_2)CF_3$$

4

$$2 + RC{\equiv}N \xrightarrow[5\text{-}7\ h]{h\nu} (CF_3)_2NCF_2N[N{=}C(Cl)R]CF_3$$

R = Cl (5), C_2F_5 (6)

In the case of the formation of 4, although the reaction follows a free radical pathway, no evidence for any other insertion products was observed. Compound 5 reacted smoothly with ClF at room temperature to give the diazane $(CF_3)_2NCF_2N[N(Cl)CF_2Cl]CF_3$ 7.

Gas phase photolysis of either $CF_3C(O)Cl$ or SF_5Cl in the presence of 2 provided good yields of diamines containing acetyl or SF_5 functional groups

$$2 + R_fCl \xrightarrow[5\text{-}7\ h]{h\nu} (CF_3)_2NCF_2N(R_f)CF_3$$

R_f = $CF_3C(O)$ (8), SF_5 (9)

The incorporation of alkoxy groups into a fluorinated diamine was attempted by reacting 1 as follows.

$$1 + LiOCH_2CF_3 \xrightarrow{-196\ ^\circ C \rightarrow RT} (CF_3)_2NC(OCH_2CF_3){=}NCF_3$$

10

Subsequent reaction with ClF at -78 °C however, resulted in breaking of the carbon-nitrogen double bond to form CF_3NCl_2 and $(CF_3)_2NCF_2OCH_2CF_3$ The latter was identified by NMR (ϕ -54.9 [$(CF_3)_2N$], -60.1 (CF_2), -74.7 (CF_3CH_2) in the ratio of 6:2:3).

Treatment of a variety of fluorinated imines with lithium alkoxides provided a method for the synthesis of azenes containing ether functionalities.

$R_fN{=}CF_2 + 2LiOR_f' \longrightarrow R_fN{=}C(OR_f')_2 + 2LiF$

R_f = CF_3; R_f' = CH_2CF_3 (11), $CH(CF_3)_2$ (12),

R_f = $(CF_3)_2N$; R_f' = CH_2CF_3 (13)

R_f = C_2F_5; R_f' = CH_2CF_3 (14)

R_f = SF_5; R_f' = CH_2CF_3 (15)

Regardless of the R_f groups present or the conditions used, reaction of these materials with ClF led only to the formation of R_fNCl_2 and $CF_2(OR_f')_2$. In the case of compound 13, one of the expected cleavage products, $(CF_3)_2NNCl_2$, was only stable at low temperatures. The compound was characterized only by the presence of a parent ion in the mass spectrum, and the rapid evolution of nitrogen at room temperature. Cleavage of the carbon-nitrogen double bond is consistent with the previously reported reactions between ClF and compounds of the type $CF_3N{=}S(R_f)_2$ ($R_f = F$, OCH_2CF_3) [18,19,20], where CF_3NCl_2 and $SF_4(R_f)_2$ are formed.

In summary, a simple, reliable high yield method for the synthesis of fluorinated diamines, as well as diazanes that contain fluorinated tertiary amino groups, has been developed. Purification is generally accomplished easily by trap-to-trap distillation. The procedures described provide a means for obtaining a variety of relatively large quantities of pure fluorinated diamines from readily synthesized or commercially available starting materials.

EXPERIMENTAL SECTION

Materials

The reagents $CF_3N{=}CF_2$ [15], $C_2F_5N{=}CF_2$ [15], $(CF_3)_2NCF{=}NCF_3$ [17], $(CF_3)_2NN{=}CCl_2$ [21], $SF_5N{=}CCl_2$ [22], and SF_5Cl [23] were prepared according to the literature methods. All other materials were purchased as indicated. chlorine monofluoride (Ozark-Mahoning); ClCN (K & K Laboratories Inc.); n-butyllithium (Aldrich); $CF_2{=}CFCl$, C_2F_5CN and $CF_3C(O)Cl$ (PCR).

General Procedures

A conventional Pyrex vacuum system equipped with a Heise Bourdon tube and Televac thermocouple gauges was used to handle gases and volatile liquids. Standard PVT techniques were used to quantify volatile products and starting materials, and trap-to-trap distillation was used for purification.

Infrared spectra were recorded with a Perkin-Elmer model 1710 Fourier transform spectrometer using 10 cm gas cells equipped with KBr windows. NMR and mass spectral data were obtained with a JEOL FX90Q Fourier transform NMR spectrometer and a VG 7070HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $(CF_3)_2NCF_2N(Cl)CF_3$ (2)

Thirty mmol of 1-[bis(trifluoromethylamino]tetrafluoro-2-aza-propene (1) and 35 mmol of ClF were condensed at -196 °C into a 75 mL stainless steel cylinder fitted with a Whitey valve and allowed to warm to room temperature. After 14 h, the resulting mixture was fractionated by trap-to-trap distillation. Compound 2 was found in ~75% yield in the -78 °C trap having passed through a -60 °C trap. Spectral data obtained are: IR (gas): 1358 s, 1324 s, 1255 s, 1224 m, 1206 s, 1084 vs, 994 m, 932 w, 851 vs, 736 w, 714 w, cm^{-1}; NMR ^{19}F ϕ -53.8 [$(CF_3)_2N$, tr, J[$(CF_3)_2N-NCF_2N$)] = 12.78], -60.11 [NCF_3, tr, J(NCF_2N-NCF_3) = 12.10], -68.8 (NCF_3N, m); CI MS [m/e (species) intensity]: 303/301 (M^+ - F) 0.08/0.23, 266 (M^+ - F - Cl) 2.88, 247 (M^+ - 2F - Cl) 16.53, 202 ($(CF_3)_2NCF_2^+$) 2.53, 134 ($CF_2NCF_3^+$ + 1) 60.48, 114 ($CF_2NCF_2^+$) 100, 69 (CF_3^+) 100. Anal. Calcd for $C_4F_{11}N_2Cl$: C, 15.0; F, 65.31. Found: C, 15.14; F, 64.9.

Preparation of 3, 4, 5, 6, 8, and 9

Four mmol of 2 and 6 mmol of CF_2CFCl, ClCN, C_2F_5CN, $CF_3C(O)Cl$ or SF_5Cl were condensed into a 500 mL quartz vessel and photolyzed with a Rayonet photochemical reactor in the gas phase for 5-7 h at a wavelength of 3000 Å. The resulting products (4, 5, 6, 8, and 9 respectively) were then purified by trap-to-trap distillation. When 2 (4 mmol) was photolyzed under the same conditions in the absence of other reactants, product 3 was obtained and similarly purified.

Characterization of compound 3

Compound 3 was obtained in 80% yield as a colorless liquid in a -65 °C trap having passed through a trap cooled to -40 °C. Spectral data obtained are: IR (gas): 1500 m, 1358 vs, 1338 s, 1271 s, 1245 s, 1224 s, 1197 m, 1146 m, 1119 m, 1042 m, 993 s, 912 m, 858 m, 816 m, 755 w, 733 m, cm^{-1}; NMR ^{19}F ϕ -53.92 [$(CF_3)_2N$, m], -60.23 (NCF_3, m), -69.0 (NCF_2N, m); EI MS [m/e (species) intensity]: 551 (M^+ - F) 2.41, 463 (M^+ - CF_3 - 2F) 1.92, 418 (M^+ - $(CF_3)_2N$) 7.77, 330 (M^+ - $(CF_3)_2NCF_2$ - 2F) 9.94, 285 ($(CF_3)_2NCF_2NCF_3^+$) 10.21, 202 ($(CF_3)_2NCF_2^+$) 100, 114 ($C_2F_4N^+$) 40.39, 69 (CF_3^+) 25.12. Anal. Calcd for $C_8F_{22}N_4$: C, 16.84; F, 73.33. Found: C, 16.4; F, 73.7.

Characterization of compound 4

Compound 4, an involatile colorless liquid was found in the quartz photolysis vessel in 70% yield. Spectral data obtained are: IR (thin film): 1359 vs, 1328 s, 1304 m, 1276 m, 1241 vs, 1224 s, 1197 s, 1146 m, 1118 w, 1085 w, 1049 w, 1014 w, 994 s, 954 w, 909 m, 847 s, 816 w, 771 m, 736 m, 718 m, 651 w, cm^{-1}; NMR ^{19}F ϕ -50.44 (CF_3N, m), -54.55 [$(CF_3)_2N$, m], -57.45 (NCF_2N, m), -60.78 (CF_2, m), -79.49 (CF, m); EI MS [m/e (species) intensity]: 403/401 (M^+ - Cl) 3.50/7.71, 247 ($(CF_3)_2NCF_2NCF^+$) 24.5, 202 ($(CF_3)_2NCF_2{}^+$) 100, 153/151 ($CF_2CFCl_2{}^+$) 35.0/47.1, 114 ($C_2F_4N^+$) 100, 103/101 ($CFCl_2{}^+$) 23.43/32.16, 69 ($CF_3{}^+$) 76.29; $d_{25^\circ C}$ = 2.17 g/ML; stability in Pyrex glass > 250 °C; stability in stainless steel, P_{O_2} = 1 atm, > 200 °C. Anal. Calcd for $C_6F_{14}N_2Cl_2$: C, 16.51; F, 61.0. Found: C, 17.0; F, 60.6.

Characterization of compound 5

This compound passed a trap cooled to -20 °C, and stopped in a trap cooled to -65 °C. It is a colorless liquid and was obtained in 68% yield. Spectral data obtained are: IR (gas). 1589 s, 1359 vs, 1348 vs, 1343 vs, 1338 vs, 1301 s, 1278 s, 1264 s, 1240 s, 1226 s, 1203 s, 1153 w, 1052 m, 993 s, 892 m, 867 m, 762 m, 735 m, 680 w, 647 m, cm^{-1}; NMR ^{19}F ϕ -53.8 [$(CF_3)_2N$, tr, J[$(CF_3)_2N$-NCF_2] = 12.26], -60.98 [NCF_3, tr, J(CF_3N-NCF_2) = 11.71], -70.48 (NCF_2N, m); EI MS [m/e (species) intensity]: 364/362 (M^+ - F) 1.71/2.13, 348/346 (M^+ - Cl) 4.2/13.36, 285 ($(CF_3)_2NCF_2NCF_3{}^+$) 2.66, 231/229 ($CF_2N(NCCl_2)CF_3{}^+$) 12.25/16.65, 202 ($(CF_3)_2NCF_2{}^+$) 100, 114 ($C_2F_4N^+$) 100, 98/96 ($NCCl_2{}^+$) 2.39/3.39, 69 ($CF_3{}^+$) 99.6. Anal. Calcd for $C_5F_{11}N_3Cl_2$: C, 15.75; F, 54.86. Found: C, 15.99; F, 55.2.

Characterization of compound 6

Having passed a trap at -10 °C, compound 6 was found in a trap cooled to -45 °C as a colorless liquid in ~65% yield. Spectral data obtained are· IR (gas): 1632 s, 1365 vs, 1305 s, 1252 vs, 1170 s, 1149 m, 1095 s, 1054 m, 1021 m, 993 s, 927 m, 900 m, 887 m, 769 m, 750 m, 595 w, 523 w, cm^{-1}; NMR ^{19}F ϕ -53.57 [$(CF_3)_2N$, tr, J[$(CF_3)_2N$-NCF_2] = 12.08], -59.19 [NCF_3, tr, J(NCF_2-NCF_3) = 12.26], -70.48 (NCF_2N, m), -81.36 (CCF_3, s), -113.34 (CCF_2, s); EI MS [m/e (species) intensity]: 430 (M^+ - Cl) 0.96, 242 ($(CF_3)_2NCF_2NNC^+$) 27.09, 202 ($(CF_3)_2NCF_2{}^+$) 100, 119 ($C_2F_5{}^+$) 59.96, 114 ($C_2F_4N^+$) 100, 69 ($CF_3{}^+$) 100. Anal. Calcd for $C_7F_{16}N_3Cl$: C, 18.06. Found: C, 18.27.

Characterization of compound 8

After passing through a -30 °C trap, compound 8 stopped in a -65 °C trap. It was obtained in 60% yield as a colorless liquid. Spectral data obtained are: IR (gas): 1890 s, 1501 m, 1369 s, 1316 s, 1270 s, 1253 s, 1221 s, 1173 m, 1130 m, 1029 w, 993 s, 942 w, 899 m, 874 m, 852 w, 815 m, 796 m, 732 s, 700 m, 555 w, cm^{-1}; NMR ^{19}F ϕ -52.58 [NCF_3, tr, J(NCF_2N-NCF_3) = 11.9], -54.49 [$(CF_3)_2N$, tr, J[$(CF_3)_2N$-NCF_2] = 12.2], -60.23 (NCF_2N, m), -56.46 [$(O)CCF_3$, s]; EI MS [m/e (species) intensity]: 285 (M^+ - $C(O)CF_3$) 6.45, 266 (M^+ - $C(O)CF_3$ - F) 3.03, 202 ($(CF_3)_2NCF_2^+$) 100, 119 ($C_2F_4N^+$) 82.31, 69 (CF_3^+) 70.33. *Anal*. Calcd for $C_6F_{14}N_2O$: C, 18.85; F, 69,63. Found: C, 17.42; F, 71.0.

Characterization of compound 9

Following photolysis and trap-to-trap distillation this compound was found in a trap at -65 °C having passed through a -40 °C trap. It was obtained in 50% yield as a colorless liquid. Spectral data obtained are: 1360 vs, 1349 vs, 1305 vs, 1256 vs, 1215 vs, 1169 s, 1140 m, 1115 m, 1093 m, 1019 w, 992 s, 926 s, 868 s, 818 s, 771 m, 753 m, 732 m, 699 w, 646 w, 603 m, 585 w, 559 w, 519 w, 482 w, 435 w, 413 w, cm^{-1}; NMR ^{19}F ϕ -49.81 (NCF_3, m), -54.85 [$(CF_3)_2N$, m], -58.32 (NCF_2N, m), +81.02, +79.23 (SF_4, d), +67.58 (SF, p); EI MS [m/e (species) intensity]: 329 (M^+ - NCF_3) 6.37, 202 ($(CF_3)_2NCF_2^+$) 1.84, 133 ($CF_2NCF_3^+$) 1.31, 127 (SF_5^+) 57.83, 114 ($C_2F_4N^+$) 70.93, 69 (CF_3^+) 100.

Preparation of compound 7

Four mmol of 5 and 6 mmol of ClF were condensed at -196 °C into a 75 mL stainless steel vessel fitted with a stainless steel valve. The contents were allowed to come to room temperature and were kept at room temperature for 12-14 h. Trap-to-trap distillation resulted in isolation of 7 (62% yield) as a colorless liquid in a -55 °C trap after passing through a trap cooled to -20 °C. Spectral data obtained are: IR (gas): 1366 s, 1339 s, 1312 s, 1246 s, 1208 s, 1191 s, 1142 s, 1111 w, 1037 s, 994 m, 947 w, 919 w, 873 w, 795 m, 723 m, 664 w, cm^{-1}; NMR ^{19}F ϕ -53.74 [$(CF_3)_2N$, tr, J[$(CF_3)_2N$-NCF_2N] = 13.0], -56.82 [NCF_3, tr, J(NCF_2N-NCF_3) = 12.88], -71.11 (NCF_2N, m), -41.46 (NCF_2Cl, m); EI MS [m/e (species) intensity]: 386/384 (M^+ - Cl) 0.2/0.89, 330 (M^+ - 2Cl - F) 1.19, 242 (M^+ - Cl - CF_2Cl -3F) 0.9, 202 ($(CF_3)_2NCF_2^+$) 100, 114 ($C_2F_4N^+$) 33.11, 87/85 (CF_2Cl^+) 0.31/1.6, 69 (CF_3^+) 21.53. *Anal*. Calcd for $C_5F_{13}N_3Cl_2$: C, 14.32; F, 58.95. Found: C, 14.62; F, 58.5.

Preparation of compound 10

To a 500 mL Pyrex round-bottomed flask containing ~10 mmol of butyllithium at -196 °C was added 10 mmol of CF_3CH_2OH. The mixture was allowed to warm slowly to room temperature. Following the removal of all volatile materials, 10 mmol of **1** was added at -196 °C. The mixture was allowed to warm slowly to room temperature and stand at room temperature for 24 h. Compound **10** (60% yield) was isolated by trap-to-trap distillation, collecting in a trap cooled to -30 °C. Spectral data obtained are: IR (gas) 2989 m, 1719 vs, 1480 m, 1457 m, 1356 s, 1256 s, 1095 vs, 994 s, 964 m, 921 m, 852 m, 765 m, 668 m, cm^{-1}; NMR ^{19}F ϕ -55.6 (NCF_3, s), -56.29 [$(CF_3)_2$, s], -73.6 [CF_3CH_2, tr, J(H-F) = 7.81]; NMR ^1H δ 4.69 (CH_2, q); CI MS [m/e (species) intensity]: 347 (M^+ + 1) 9.23, 327 (M^+ - F) 66.86, 247 (M^+ - OCH_2CF_3) 4.75, 194 (M^+ - $N(CF_3)_2$) 40.52, 159 ($C_3F_5N_2^+$) 3.54, 83 (CF_3N^+) 22.29, 81 ($CF_2CH_2O^+$ + 1) 100, 69 (CF_3^+) 29.41.

Preparation of 11, 12, 13, 14, and 15

To a dry 500 mL Pyrex round-bottomed flask, equipped with a Kontes Teflon stopcock, 4 mL (~10 mmol) of 2.5 M butyllithium in hexane was added under a nitrogen atmosphere. The vessel was evacuated at -196 °C and an excess (~12 mmol) of the alcohol [CF_3CH_2OH or $(CF_3)_2CHOH$] was condensed into the flask. The mixture was allowed to warm slowly (in a cold Dewar) to room temperature and left at room temperature for 2 to 4 h. All volatiles were removed under vacuum, and the remaining solid R_fOLi was cooled to -196 °C. Five mmol of $CF_3N{=}CF_2$, $(CF_3)_2NN{=}CCl_2$, $C_2F_5N{=}CF_2$ or $SF_5N{=}CCl_2$ was then condensed into the flask. The mixture was allowed to warm to room temperature over a 2 h period and stand at room temperature for 24 h. The resulting mixtures were separated by trap-to-trap distillation to give compounds **11** and **12**, **13**, **14**, and **15** respectively.

Characterization of compound 11

This compound was isolated in a cold trap at -45 °C in 75% yield. Spectral data obtained are: IR (gas): 2988 w, 2950 w, 1713 vs, 1423 m, 1357 m, 1289 s, 1263 s, 1190 vs, 1085 vs, 990 w, 968 w, 932 w, 846 vs, 739 w, 666 w, cm^{-1}; NMR ^{19}F ϕ -53.75 (CF_3N, s), -74.01 [CF_3CH_2, tr, J(H-F) = 8.05]; NMR ^1H δ 4.64 (CH_2, q); CI MS [m/e (species) intensity]: 295 (M^+ + 2) 2.76, 294 (M^+ + 1) 35.36, 293 (M^+) 12.28, 274 (M^+ - F) 100, 194 (M^+ - OCH_2CF_3) 9.05, 163 ($C_3F_5NH_2O^+$) 35.32, 112 (CF_3NCO^+ + 1) 60.85, 83 ($CF_3CH_2^+$) 58.7, 69 (CF_3^+) 30.56. Anal. Calcd for $C_6F_9NH_4O_2$: C, 24.57; F, 58.36; H, 1.37. Found: C, 24.74; F, 58.4; H, 1.36.

Characterization of compound 12

Compound 12 was found in a trap cooled to -40 °C in ~72% yield Spectral data are: IR (gas): 3015 w, 2991 m, 1734 vs, 1381 s, 1363 s, 1344 s, 1278 vs, 1249 s, 1218 s, 1196 s, 1123 s, 1098 m, 1034 m, 997 s, 914 m, 890 m, 760 m, 728 m, 693 m, cm^{-1}; NMR ^{19}F ϕ -54.85 (CF_3N, s), -73.26 [$(CF_3)_2CH$, d, J(H–F) = 5.25]; NMR ^1H δ 5.71 (CH, spt); CI MS [m/e (species) intensity]: 430 (M^+ + 1) 7.03, 429 (M^+) 8.8, 410 (M^+ - F) 100, 262 (M^+ - $OCH(CF_3)_2$) 5.97, 151 ($(CF_3)_2CH^+$) 18.85, 112 ($C_3F_4^+$) 34.91, 69 (CF_3^+) 71.01. Anal. Calcd for $C_8F_{15}H_2NO_2$: C, 22.38; N, 3.26; H, 0.47. Found: C, 23.01; N, 3.37; H, 0.57.

Characterization of compound 13

This compound was isolated in a trap held at -30 °C in 70% yield. Spectral data obtained are: IR (gas): 3039 w, 2988 m, 1664 vs, 1464 m, 1427 s, 1370 s, 1314 s, 1261 s, 1174 vs, 1081 s, 1064 s, 972 s, 841 m, 755 m, 729m, 654 m, cm^{-1}; NMR ^{19}F ϕ -64.92 [$(CF_3)_2N$, s], -74.13 and -74.71 [(CF_3CH_2), tr, J(H–F) = 7.8]; NMR ^1H δ 4.69 (CH_2, q); CI MS [m/e (species) intensity]: 378 (M^+ + 2) 2.16, 377 (M^+ + 1) 27.18, 376 (M^+) 43.49, 357 (M^+ - F) 100, 277 (M^+ - OCH_2CF_3) 10.31, 163 ($C_3F_5NH_2O^+$) 19.48, 83 (CF_3CH_2) 75.69, 69 (CF_3^+) 41.18. Anal. Calcd for $C_7F_{12}N_2H_4O_2$: C, 22.34; F, 60.64; H, 1.06. Found: C, 22.58; F, 60.0; H, 1.22.

Characterization of compound 14

A trap at -45 °C was found to contain a 70% yield of compound 14. Spectral data obtained are: IR (gas): 2968 m, 2881 w, 1689 vs, 1462 m, 1425 s, 1355 s, 1279 s, 1256 s, 1177 vs, 1102 m, 1073 m, 1048 m, 965 m, 936 w, 862 w, 841 w, 749 m, 696 w, 662 w, 539 w, cm^{-1}; NMR ^{19}F ϕ -73.89 [CF_3, tr, J(H–F) = 7.8], -86.52 (CF_3, s), -94.34 (CF_2, s); NMR ^1H δ 4.80 (CH_2, q); CI MS [m/e (species) intensity]: 344 (M^+ + 1) 11.07, 324 (M^+ - F) 100, 274 (M^+ - CF_3) 30.88, 244 (M^+ - OCH_2CF_3) 5.64, 163 ($C_3F_5NH_2O^+$) 14.68, 83 ($CF_3CH_2^+$) 45.49, 69 (CF_3^+) 7.28.

Characterization of compound 15

This compound was found in a trap cooled to -30 °C. It was obtained in 65% yield. Spectral data obtained are: IR (gas): 2979 m, 1678 vs, 1459 m, 1425 s, 1357 m, 1284 s, 1256 m, 1176 vs, 1144 s, 1065 m, 1013 m, 964 s, 877 s, 817 m, 760 m, 685 m, 597 s, cm^{-1}; NMR ^{19}F ϕ +79.9 (SF, p), +73.0 (SF_4, d), -73.89 [CF_3, tr, J(H-F) = 7.63], -74.18 [CF_3, tr, J(H-F) = 8.24]; NMR ^1H δ 4.63 (CH_2, q), 4.07 (CH_2, q); CI MS [m/e (species) intensity]: 352 (M^+ + 1) 3.13, 351 (M^+) 5.12, 332 (M^+ - F) 100, 252 (M^+ - OCH_2CF_3) 3.0, 163 ($C_3F_5NH_2O^+$) 24.91, 127 (SF_5^+) 22.74, 99 ($OCH_2CF_3^+$) 28.43, 83 ($CH_2CF_3^+$) 95.6, 69 (CF_3^+) 11.79.

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