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Some reactions of fluorinated azaalkenes, $R_fN=CF_2$

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Abstract

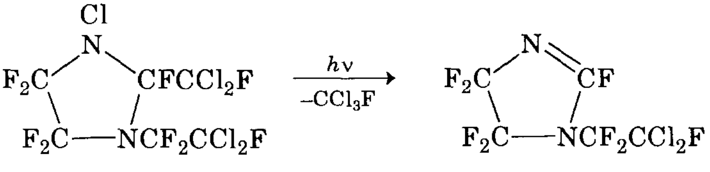
More facile routes to fluorinated azaalkenes encourage further studies of the reactions of these compounds. Reactions of $(CF_3)_2NCF_2N=CF_2$ with lithiated polyfluoroalkoxides give $(CF_3)_2NCF_2N=CF_{2-x}(OR_f)_x$ [$X=1$ or 2; $R_f=CF_3CH_2$, $(CF_3)_2CH$ or $(CF_3)_2C(CH_3)$]. Chlorine fluoride can be added to the nitrogen–carbon double bond of these mono- and bis-alkoxides with retention of the molecular backbone to give $(CF_3)_2NCF_2N(Cl)CF_{3-x}(OR_f)_x$ [$X=1$ or 2; $R_f=CF_3CH_2$, $(CF_3)_2CH$ or $(CF_3)_2C(CH_3)$]. Photolysis of neat $NF_2CXFCF_2NCl_2$, which results from chlorofluorination of $F_2NCXFCN$ ($X=Cl$ or F), gives diazenes $[F_2NCXFCF_2N=]_2$. Thermolysis of $F_2NCF_2CF_2NCl_2$ in a 1:1 ratio with $CF_2=CClF$ results in $F_2NCF_2CF_2N(Cl)CF_2CCl_2F$. Upon photolysis of the latter, a new azaalkene, $F_2NCF_2CF_2N=CF_2$ results. Following chlorofluorination of $F_2NCF_2CF_2N=CF_2$, insertion of ClCN or F_2NCF_2CN into the resulting nitrogen–chlorine bond gives imines $F_2NCF_2CF_2N(CF_3)N=CCl_2$ and $F_2NCF_2CF_2N(CF_3)N=C(Cl)CF_2NF_2$. Successive chlorofluorination of the latter compound with intramolecular elimination of chlorine, followed by photolysis, gives rise to a stable, non-volatile tetrazane (70%) that contains eight nitrogen atoms, $F_2NCF_2CF_2N(CF_3)N(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF_2CF_2NF_2$.

Introduction

Fluorinated azaalkenes are well-studied compounds and their syntheses and chemistry have attracted considerable attention [1]. Previously published routes to per- or polyfluoroazaalkenes often require high temperature and/or subsequent fluorination or the yields may be low. Recently we reported and continue to utilize a convenient, facile route for the high-yield preparation of azaalkenes by photolysis of selected chloro(perfluoroalkyl)(chlorofluoroalkyl)amines, $R_fN(R_f')Cl$, with concomitant loss of C-1 chlorofluorocarbons, or chlorine [2]. For example, photolysis of the monochloroamines [2]:

$$R_fN(CF_2CClXF)Cl \xrightarrow{h\nu} R_fN=CF_2 + CCl_2XF$$

where $X=Cl$ or F as well as the heterocyclic chloroamines [3]:



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gives high yields of azaalkenes, via the loss of CF_2Cl_2 or CCl_3F. In some instances when the terminal carbon-containing substituent β to the N−Cl moiety is highly fluorinated, azaalkene formation is accompanied by loss of chlorine, e.g., from refs. 4 and 5 respectively:

$$CF_3(CF_3CF_2)NN(Cl)CClFCF_3 \xrightarrow[-Cl_2]{h\nu} CF_3(CF_3CF_2)NN{=}CFCF_3$$

$$CF_3N(Cl)CF_2CF_2N(Cl)CF_3 \xrightarrow[-Cl_2]{h\nu} 2CF_3N{=}CF_2$$

In this paper, we wish to report the syntheses of some new azaalkenes and some reactions of azaalkenes which take advantage of the reactivity of the carbon–nitrogen double bond or the carbon–fluorine bonds at the azene carbon. Additionally, it now has been possible to synthesize a stable tetraazane that contains eight nitrogen atoms.

Earlier, in these laboratories, a powerful route to the synthesis of dichloro(perfluoroalkyl)amines and dichloro(perfluoroalkyl)amides, R_fNCl_2 and $R_fC(O)NCl_2$ was discovered when the appropriate imidosulfurous difluorides were reacted with chlorine fluoride [6]:

$$R_fN{=}SF_2 + \text{excess ClF} \longrightarrow R_fNCl_2 + SF_4$$

or

$$R_fC(O)N{=}SF_2 + \text{excess ClF} \longrightarrow R_fC(O)NCl_2 + SF_4$$

In an effort to determine the effect that less-electronegative substituents bonded to sulfur would have on the products when $R_fN{=}SX_2$ $(X \neq F)$ were reacted with chlorine fluoride, we synthesized a variety of bis(polyfluoroalkyl)(trifluoromethyl)imidosulfites. Regardless of stoichiometry, chlorine fluoride oxidatively fluorinated the sulfur(IV) compounds to a new family of *cis/trans*-sulfur hexafluoride derivatives with concomitant severing of the nitrogen–sulfur bond to form R_fNCl_2 [7].

$$R_fN{=}S(OR_f)_2 + 4ClF \xrightarrow[10\ \text{h}]{-78\ ^\circ\text{C}} R_fNCl_2 + (R_fO)_2SF_4 + Cl_2$$

Results and discussion

When an improved route to azaalkenes was found, it was of interest to compare the behaviour of these materials with that of their sulfur analogues. It is well established that chlorine fluoride saturates the carbon–nitrogen double bond to give stable but reactive products, e.g.:

$$C_2F_5N{=}CF_2 + ClF \longrightarrow C_2F_5(CF_3)NCl$$

We and others have exploited the chemistry of the nitrogen–chlorine bond in these compounds and this is discussed in more detail below.

The question then was if carbon–nitrogen bond breaking does not occur when the azaalkene is totally fluorinated, what would the impact of chlorine fluoride be if the $=CF_2$ group were replaced by $=CFR_f'$ or $=C(R_f')_2$? To investigate this query, several azenes were reacted with lithium alkoxides, *viz.* [8]:

$$R_fN{=}CF_2 + 2LiOR'_f \longrightarrow R_fN{=}C(OR'_f)_2 + 2LiF$$

where $R_f = CF_3$; $R'_f = CH_2CF_3$ or $CH(CF_3)_2$, $R_f = (CF_3)_2N$; $R'_f = CH_2CF_3$, $R_f = C_2F_5$; $R'_f = CH_2CF_3$, $R_f = SF_5$; $R'_f = CH_2CF_3$. Independent of the R_f group or the R'_f group or the conditions used, reaction of these materials with ClF led only to breaking of the nitrogen–carbon bond with formation of R_fNCl_2 and $CF_2(OR'_f)_2$. This is identical to the $R_fN{=}S(OR'_f)_2$/chlorine fluoride reactions. However, in the present work, we can now report that when the substituent group bound to nitrogen (R_f) is $(CF_3)_2NCF_2$, the chlorine fluoride reactions change markedly.

The thermally induced insertion of $CF_2{=}CClF$ into a single nitrogen–chlorine bond of $(CF_3)_2NCF_2NCl_2$ gives rise to $(CF_3)_2NCF_2N(Cl)CF_2CCl_2F$ which, when photolyzed, forms $(CF_3)_2NCF_2N{=}CF_2$ (80% yield) [9]. Reactions of the azene with lithiated polyfluoroalkoxides can be controlled to prepare the mono- and di-substituted ether azenes:

$$(CF_3)_2NCF_2N{=}CF_2 \xrightarrow[\substack{-196\ ^\circ\mathrm{C}\ \mathrm{to}\ 25\ ^\circ\mathrm{C} \\ 25\ ^\circ\mathrm{C}\ 30\ \mathrm{h}}]{LiOR_f} (CF_3)_2NCF_2N{=}CF_{2-x}(OR_f)_x$$

for

R_f	X=1 (yield)	X=2 (yield)
CF_3CH_2	**1** (60%)	**2** (24%)
$(CF_3)_2CH$	**3** (50%)	**4** (25%)
$(CF_3)_2C(CH_3)$	**5** (68%)	**6** (6%)

These new compounds are stable, colorless, volatile liquids. When compounds **1** to **6** are exposed to chlorine fluoride, it is found that addition to the $N{=}CFOR_f$ or $N{=}C(OR_f)_2$ polar bond occurs smoothly to form a new family of monochloroamines with mono- or diether substituents:

$$(CF_3)_2NCF_2N{=}CF_{2-x}(OR_f)_x \xrightarrow[\substack{\text{stainless} \\ \text{steel}}]{ClF} (CF_3)_2NCF_2N(Cl)CF_{3-x}(OR_f)_x$$

R_f	X=1	X=2
CF_3CH_2	**7** (25%)	**8** (67%)
$(CF_3)_2CH$	**9** (80%)	**10** (79%)
$(CF_3)_2C(CH_3)$	**11** (60%)	–

A slight excess of ClF was added at −196 °C and the mixture was warmed slowly to −60 °C for 12 h and then warmed from −40 °C to 5 to 10 °C over 12 h. The mixtures were separated by trap-to-trap distillation under dynamic vacuum. These volatile compounds are stable and their reaction chemistry is being examined. It is surprising that this family of highly substituted azenes is stable toward ClF addition, since from all points of comparison the difference between these compounds and the ones reported earlier seems very small [8].

Routes to the precursors of fluorinated azaalkenes can be circuitous but very often involve the utilization of fluorinated nitriles as the starting point. The high-yield syntheses of difluoroaminodifluoroacetonitrile, NF_2CF_2CN [10, 11], and difluoroaminochlorofluoroacetonitrile, $NF_2CClFCN$ [11] provides a readily available source of reactive starting materials. The reaction:

$$CXF{=}CH_2 + N_2F_4 \xrightarrow[KF]{\Delta} F_2NCXFCN + 2HF$$

where X = F, **12** [10]; Cl, **13** [11] proceeds via the addition of the $\cdot NF_2$ radical across the olefin linkage with subsequent loss of HF.

The facile addition of ClF across the triple bond of the nitrile gives the dichloroamino derivatives [10, 12–14] which are useful synthetic reagents that react readily via insertion or intermolecular halogen elimination reactions [2–5, 8–10]:

$$\mathbf{12} \text{ or } \mathbf{13} \xrightarrow{ClF} F_2NCXFCF_2NCl_2$$

where X = F, **14** [10]; Cl, **15**. In both **13** and **15** there is a chiral center at CX and two magnetically non-equivalent diastereotopic fluorine atoms bonded to nitrogen as well as two magnetically non-equivalent fluorine atoms in $-CF_2NCl_2$. For **15**, the ^{19}F NMR spectrum is a five spin, ABXA′B′. A low-resolution analysis of the spectrum was earlier achieved since the ratios $\Delta\nu_{AB}/J_{AB}$ (0.78), $\Delta\nu_{A'B'}/J_{A'B'}$ (3.46) and the J values, $J_{AB} \gg J_{A'B'} \gg J_{BA'}$, etc., were appropriate for the observed perfectly symmetrical AB and A′B′ quartets [11]. High-resolution analysis was more difficult partly because of the nitrogen quadrupole which precludes resolution of the fine splitting for $AB(NF_A{-}NF_B)$. However, the carbon fluorine position of the spectrum was well resolved. Through the use of the PMR computer program from Serena Software, it was possible to simulate the experimentally observed spectrum. The infrared spectrum of **15** was found to contain appropriate N−F, N−Cl and CF_2 stretching frequencies.

Upon photolysis, **14** and **15** gave their respective diazenes:

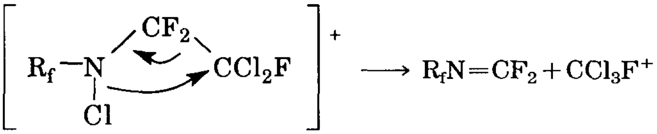
$$\mathbf{14} \text{ or } \mathbf{15} \xrightarrow{h\nu} (F_2NCXFCF_2N{=})_2$$

where X = F, **16** [10]; Cl, **17** [11]. These diazenes are highly stable and tend to have less complex ^{19}F NMR spectra than **14** or **15**. When **14** was thermalized with olefins in a 1:1 ratio, the *N*-chloro precursor to the azaalkene was obtained

$$\mathbf{14} + CF_2{=}CFCl \xrightarrow{\Delta} \underset{(\mathbf{18})}{F_2NCF_2CF_2N(Cl)CF_2CCl_2F}$$

Interestingly, in the chemical ionization mass spectrum of **18**, while the largest peak at *m/e* 333 can be assigned to $(M^+ - F)$, the base peak at *m/*

e 101 arises from CCl_2F^+, which suggests the following rearrangement has occurred in the mass spectrometer [11]:



A similar rearrangement must occur upon photolysis as well. In fact, photoelimination reactions of **18** do result in high yields of the azaalkene **19**

$$\mathbf{18} \xrightarrow{h\nu} F_2NCF_2CF_2N{=}CF_2$$

(19)

As is typical of azaalkenes, the $N{=}CF_2$ group has non-equivalent fluorine atoms in the ^{19}F NMR spectrum. Compound **19** was heated at 32 °C without coalescence of the C—F resonance having occurred in the NMR. Because of the unpredictability of difluoroamino-containing compounds, efforts which would have involved further heating were discontinued.

The photolysis of **18** gave rise to a reactive azaalkene which, for the first time, contains the difluoroamino group. Taking advantage of **19** as a precursor to further NF_2-containing compounds, chlorine fluoride was first added to the double bond, *viz.*:

$$\mathbf{19} + ClF \longrightarrow F_2NCF_2CF_2N(Cl)CF_3$$

(20)

Upon photolysis, the nitriles ClCN and NF_2CF_2CN were readily inserted into the N—Cl bond to yield interesting imines:

$$F_2NCF_2CF_2N(Cl)CF_3 + ClCN \xrightarrow{h\nu} F_2NCF_2CF_2N(CF_3)N{=}CCl_2$$

(21)

and

$$F_2NCF_2CF_2N(Cl)CF_3 + NF_2CF_2CN \xrightarrow{h\nu} F_2NCF_2CF_2N(CF_3)N{=}C(Cl)CF_2NF_2$$

(22)

In **21** and **22**, the stretching frequences in the infrared spectrum for the carbon–nitrogen double bond, $\rangle C{=}N{-}$, are assigned at 1585 and 1631 cm^{-1}, respectively. In **21**, the ^{19}F NMR spectrum has become simpler in that the resonance band observed at ϕ -59.8 assigned to CF_3 is a well-defined triplet of triplets. In compound **22**, all resonances are singlets with the exception of CF_3 and the vicinal CF_2 groups which are coupled.

Successive chlorine fluoride additions with subsequent intramolecular elimination of chlorine with **22** gave rise finally to a new stable tetraazane that contains eight nitrogen atoms:

$$\mathbf{22} + ClF \longrightarrow F_2NCF_2CF_2N(CF_3)N(Cl)CClFCF_2NF_2$$

(23)

$$\xrightarrow[-Cl_2]{h\nu} F_2NCF_2CF_2N(CF_3)N{=}CFCF_2NF_2 \xrightarrow{ClF}$$

(24)

$$F_2NCF_2CF_2N(CF_3)N(Cl)CF_2CF_2NF_2 \xrightarrow[-Cl_2]{h\nu}$$

(25)

$$F_2NCF_2CF_2N(CF_3)N(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF_2CF_2NF_2$$

(26) (70%)

Compound **23** is easily induced to lose chlorine either thermally or photolytically to form the azaalkene **24** which readily adds chlorine fluoride to give **25**. In this instance, photolysis results in the loss of chlorine and coupling of the nitrogen-containing fragments to form the stable, involatile tetrazane **26**. The existence of these high nitrogen compounds is supported by spectral data and elemental analysis.

We are continuing our study of the characteristics exhibited by high nitrogen compounds which contain a variety of functional groups, as well as varying ratios of fluorine and nitrogen. Similarly, structure/stability relationship as well as changes in physical properties as a function of structure in polyfluorinated amines, *N*-chloroamines and polyamines are being explored.

Experimental

Materials

The starting materials $CF_2{=}CFCl$, CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_2CCH_3OH$ (PCR), $CF_2{=}CH_2$, $CFCl{=}CH_2$, n-butyl lithium (Aldrich) and ClF (Ozark–Mahoning) were purchased and used as received. The azaalkenes $CF_3N{=}CF_2$ and $(CF_3)_2NCF_2N{=}CF_2$ were prepared by the literature methods [9].

General procedures

The vacuum system used to transfer volatile materials consisted of a Pyrex glass vacuum line equipped with a Heise Bourdon tube and Televac thermocouple gauges. A Perkin-Elmer Model 1710 IR Fourier transform spectrometer and an IBM PS/2 data station were used to obtain the IR spectra. ^{19}F and ^{1}H NMR spectra were recorded in $CDCl_3$ on either a JEOL FX-90 Q or an IBM NL 200 Fourier transform NMR spectrometer with CCl_3F and $(CH_3)_4Si$ as references, respectively. Positive shifts are downfield from the reference. Mass spectral data were obtained with a VS 7070 mass spectrometer, and a Rayonet reactor with 3000 Å UV lamps was used for photochemical reactions. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Preparation of $(CF_3)_2NCF_2N{=}CF(OR_f)$ and $(CF_3)_2NCF_2N{=}C(OR_f)_2$ [$R_f{=}OCH(CF_3)_2$, OCH_2CF_3 or $OCCH_3(CF_3)_2$]

To a dry 500 ml Pyrex round-bottomed flask equipped with a Kontes Teflon stopcock, was added 10 mmol of butyl lithium in hexane under a nitrogen atmosphere. The vessel was evacuated at −196 °C, and 12 mmol of the alcohol was added to the flask. The reaction mixture was allowed to warm slowly to room temperature and stand at that temperature for 2 to 4 h. Following the removal of all volatiles under vacuum, the solid residue was held at −196 °C and 10 or 20 mmol of $(CF_3)_2NCF_2N{=}CF_2$ was condensed into the flask. The mixture was allowed to warm to room temperature over a period of 2 h. After stirring at room temperature for 24 to 40 h, the products were separated by low temperature trap-to-trap distillation.

Characterization of $(CF_3)_2NCF_2N{=}C(F)OCH_2CF_3$ *(1)*

By low-temperature trap-to-trap distillation, this compound was isolated in a trap cooled to −60 °C (60% yield) having passed through a trap at −40 °C. Spectral data obtained were: IR (gas): 2982w, 1769s, 1397s, 1358s, 1264vs, 1197vs, 1098vs, 1027m, 998s, 965w, 925w, 847vw, 786vw, 757w, 718w, 657w, 576w, 548w, 482w cm^{-1}; ^{19}F NMR ϕ −57.2 [$(CF_3)_2N$, q], $J[(CF_3)_2N{-}CF_3] = 3.2$ Hz, −74.6, (CF, t), $J(CF{-}H) = 7.8$ Hz, −78.0 (CF, t), $J(CF{-}H) = 8.6$ Hz, −56.5 (CF_3, hpt); ^{1}H NMR δ 4.63 (CH_2, m), $J(CF_3{-}H) = 7.8$ Hz; CI MS [*m*/*e* (species) intensity]: 347 ($M^+ + 1$) 12.2, 327 ($M^+ - F$) 100, 248 ($M^+ + 1 - OCH_2CF_3$) 29.7, 247 ($M^+ - OCH_2CF_3$) 10.1, 239 ($CF_2NCF_2NCOCH_2CF_3{}^+$) 10.5, 194 [$CF_2NC(F)OCH_2CF_3{}^+$] 75.7, 179 [$(CF_3)_2NCN^+ + 1$] 25.6, 157 ($C_4F_5N^+$) 9.3, 134 ($CF_3NCF_2{}^+ + 1$) 2.8, 114 ($CF_2NCF_2{}^+$) 3.3, 83 ($CF_3CH_2{}^+$) 63.8, 69 ($CF_3{}^+$) 81.5.

Characterization of $(CF_3)_2NCF_2N{=}C(OCH_2CF_3)_2$ *(2)*

The compound $(CF_3)_2NCF_2N{=}C(OCH_2CF_3)_2$ was found in 23.8% yield in a trap cooled to −20 °C having passed a trap cooled to 0 °C. Spectral data obtained were: IR (gas): 2986w, 1715vs, 1421s, 1357vs, 1333vs, 1289vs, 1247vs, 1193vs, 1148s, 1100s, 1073m, 1036s, 997s, 967m, 885m, 862m, 758m, 671m, 583m, 571m, 554w, 481w cm^{-1}; ^{19}F NMR ϕ −54.2 [$(CF_3)_2N$, m], −56.8 (CF_2, m), −74.5 (CF_3, m); ^{1}H NMR δ 4.6 (CH_2, m); CI MS [*m*/*e* (species) intensity]: 427 ($M^+ + 1$) 4.1, 407 ($M^+ - F$) 41.6, 327 ($M^+ - -OCH_2CF_3$) 38.3, 294 ($C_6F_9H_4NO_2{}^+ + 1$) 19.4, 275 [$CF_2NC(OCH_2CF_3)_2{}^+ + 1$] 12.3, 274 [$CF_2NC(OCH_2CF_3)_2{}^+$] 100, 227 ($CF_2NCF_2NOCH_2CF_3{}^+$) 41.6, 207 ($CF_2NCF_2NOCHCF_2{}^+$) 73.4, 149 ($C_4F_2H_3N_2O_2{}^+$) 44.7, 127 ($CF_3CH_2OCO^+$) 44.1, 112 ($CF_3CH_2OC^+ + 1$) 36.4, 92 ($CF_2NCO^+$) 14.8, 83 ($CF_3CH_2{}^+$) 100, 69 ($CF_3{}^+$) 68.5.

Characterization of $(CF_3)_2NCF_2N{=}C(F)OCH(CF_3)_2$ *(3)*

The product was obtained in 50% yield in a trap cooled to −60 °C having passed through a trap held at −30 °C. Spectral data obtained were: IR (gas): 2994m, 1732vs, 1364vs, 1322vs, 1252vs, 1173s, 1121vs, 1102vs, 1042s, 998vs, 933s, 914m, 881w, 787w, 761s, 727m, 694s, 649w, 616vw cm^{-1}; ^{19}F NMR ϕ −57.0 [$(CF_3)_2N$, m], −56.8 (CF_2, m), −73.6 (CF_3, m); ^{1}H NMR δ 5.8 (CH, m); CI MS [*m*/*e* (species) intensity]: 415 ($M^+ + 1$) 13.8, 395 ($M^+ - F$) 100, 375 ($M^+ - HF_2$) 8.1, 307 ($CF_2NCF_2NCOCH(CF_3)_2{}^+$) 8.5, 262 ($CF_2NC(F)OCH(CF_3)_2{}^+$) 99, 217 [$(CF_3)_2NCF_2N^+ + 1$] 88, 197 [$(CF_3)_2NCFN^+$] 5.8, 179 [$(CF_3)_2CHOC^+$] 51.3, 151 [$(CF_3)_2CH^+$] 61.4, 134 ($CF_3NCF_2{}^+ + 1$) 6.6, 112 ($C_3F_4{}^+$) 39.0, 69 ($CF_3{}^+$) 100.

Characterization of $(CF_3)_2NCF_2N{=}C(OCH(CF_3)_2)_2$ *(4)*

A 25% yield of this product was isolated in a trap cooled to −30 °C having passed though a trap cooled to −10 °C. Spectral data obtained were: IR (gas): 2994m, 1732vs, 1364vs, 1322vs, 1252vs, 1173s, 1121vs, 1102vs, 1042s, 998vs, 933s, 914m, 881w, 787w, 761s, 727m, 694s, 649w, 616w cm^{-1}; ^{19}F NMR ϕ −54.3 [$(CF_3)_2N$, m], −56.8 (CF_2, m), −73.5 [$(CF_3)_2C$]; ^{1}H NMR δ 7.96 (CH, m), 4.34 (CH, m); CI MS [*m/e* (species) intensity]: 543 ($M^+ - F$) 3.1; 523 ($M^+ - HF_2$) 1.0, 410 [$M^+ - (CF_3)_2N$] 21.8, 395 [$M^+ - OCH(CF_3)_2$] 50.4, 375 [$M^+ - OCH(CF_3)_2 - HF$] 1.4, 307 [$CF_2NCF_2NCOCH(CF_3)_2{}^+$] 7.8, 262 ($C_5HF_9NO^+$) 32.4, 248 ($C_5HF_9O^+$) 7.8, 217 [$(CF_3)_2NCF_2N^+ + 1$] 3.2, 197 [$(CF_3)_2NCFN^+$) 1.7, 179 ($C_3F_6N_2{}^+ + 1$) 13.7, 151 [$(CF_3)_2CH^+$] 16.7, 134 ($CF_3NCF_2{}^+ + 1$) 2.5, 112 ($C_3F_4{}^+$) 10.6, 69 ($CF_3{}^+$) 100.

Characterization of $(CF_3)_2NCF_2N{=}C(F)OCCH_3(CF_3)_2$ *(5)*

The product was isolated by low-temperature trap-to-trap distillation in 68% yield in a trap cooled to −50 °C having passed through a trap cooled to −10 °C. Spectral data obtained were: IR (gas): 1763vs, 1392vs, 1332vs, 1249vs, 1196vs, 1176vs, 1132s, 1097s, 1038m, 1003s, 958m, 878m, 843m, 830m, 763m, 752m, 727m, 702m, 636w, 573w, 540w, 481w, 456w cm^{-1}; ^{19}F NMR ϕ −55.6, [$(CF_3)_2N$, d], $J[(CF_3)_2N{-}CF] = 13.18$ Hz, −49.8 (CF_2, d), $J(CF_2{-}CF) = 9.4$ Hz, −20.5 (CF, m), −78.2 [$(CF_3)_2C$, m]; ^{1}H NMR δ 1.9 (CH_3, s); CI MS [*m/e* (species) intensity]: 429 ($M^+ + 1$) 4.4, 409 ($M^+ - F$) 41.0, 343 ($M^+ - CH_3 - CF_3 - H$) 3.9, 276 [$M^+ - (CF_3)_2N$] 25.9, 247 [$M^+ - OC(CH_3)(CF_3)_2$] 93.1, 231 ($C_5F_8H_3O^+$) 37.9, 202 [$(CF_3)_2NCF_2{}^+$] 23.7, 159 ($C_3F_5N_2{}^+$) 31.1, 145 ($C_3F_5N^+$) 100, 114 ($CF_2NCF_2{}^+$) 28.8, 112 ($C_3F_4{}^+$) 30.7, 95 ($C_3F_3H_2{}^+$) 14.5, 77 ($C_3F_2H_3{}^+$) 21.9, 69 ($CF_3{}^+$) 100.

Characterization of $(CF_3)_2NCF_2N{=}C[OCCH_3(CF_3)_2]_2$ *(6)*

Following low-temperature trap-to-trap distillation, this product was found in 6.4% yield in a trap cooled to −25 °C. Spectral data obtained were: IR (liq): 2970m, 1710vs, 1397s, 1218vs, 998s, 956w, 888s, 879s, 858s, 810vw, 798vw, 701s, 674m, 538s, 493s, 455s, 451vs, 446vs, 428s, 417vs, 407s cm^{-1}; ^{19}F NMR ϕ −56.1 [$(CF_3)_2N$, m], −54.7 (CF_2, m), −79.8 [$(CF_3)_2C$, m]; ^{1}H NMR δ 2.1 (CH_3, m); CI MS [*m/e* (species) intensity]: 571 ($M^+ - F$) 2.3, 520 ($M^+ - CF_3 - H$) 6.0, 438 [$M^+ - (CF_3)_2N$] 26.1, 409 [$M^+ - OCCH_3(CF_3)_2$] 9.1, 387 [$N{=}C(OCCH_3(CF_3)_2OCCH_2(CF_3)_2{}^+$] 14.0, 165 [$CCH_3(CF_3)_2{}^+$] 16.8, 145 ($C_4F_5H_2{}^+$) 100, 69 ($CF_3{}^+$) 60.0.

Preparation of $(CF_3)_2NCF_2N(Cl)CF_2OR_f$ *and* $(CF_3)_2NCF_2N(Cl)CF(OR_f)_2$ $[R_f = CH_2CF_3$, $CH(CF_3)_2$ *or* $CCH_3(CF_3)_2]$

Typically 4 mmol of $(CF_3)_2NCF_2N{=}C(F)OR_f$ or $(CF_3)_2NCF_2N{=}C(OR_f)_2$ and 5 mmol of ClF were condensed (at −196 °C) into a 75 ml stainless steel vessel fitted with a Whitey valve. The mixture was held at −60 °C for 12 h, and subsequently warmed over a period of 12 h from −40 °C to approximately 10 °C. The resulting products were then separated by low-temperature trap-to-trap distillation.

Characterization of $(CF_3)_2NCF_2{}^ANCl)CF_2{}^BOCH_2CF_3$ *(7)*

A 25% yield of this product was found in a trap cooled to −40 °C having passed through a trap cooled to −15 °C. Spectral data obtained were: IR (gas): 2985w, 1351vs, 1327vs, 1300vs, 1269s, 1235vs, 1216vs, 1188vs, 1098w, 1075m, 1029vs, 1004m, 975m, 931w, 914w, 873w, 734s, 660w, 625w, 566w, 534w, 523w, 481w cm^{-1}; ^{19}F NMR ϕ −53.1 [$(CF_3)_2N$, t], $J[(CF_3)_2N-CF_2(A)] = 16.0$ Hz, −54.6 [CF_2(A), m], −59.2 [(CF_2(B), m], −74.8 (CF_3CH_2, m); ^{1}H NMR δ 4.2 (CH_2, m); CI MS [*m/e* (species) intensity] (observed isotopic ratios were correct): 381 ($M^+ - F$) 4.3, 347 ($M^+ + 1 - ClF$) 19.0, 327 ($M^+ - ClF_2$) 100, 296 ($M^+ - CF_3 - Cl$) 7.0, 276 ($M^+ - CF_3 - Cl - HF$) 99.8, 260 ($C_4ClF_7N_2O^+$) 72.5, 247 [$(CF_3)_2NCF_2NCF^+$] 57.4, 194 ($CF_3CH_2OCF_2NCF^+$) 99.0, 149 ($CF_3CH_2OCF_2{}^+$) 98. Analysis: Calcd. for $C_6ClF_{13}H_2N_2O$: C, 18.00; H, 0.50; F, 61.75%. Found: C, 18.72; H, 0.55; F, 61.15%.

Characterization of $(CF_3)_2NCF_2N(Cl)CF(OCH_2CF_3)_2$ *(8)*

This compound was found in a −45 °C trap having passed through a trap cooled to −20 °C (66.0% yield). Spectral data obtained were: IR (gas): 1351s, 1327s, 1299s, 1268s, 1236s, 1216s, 1157vs, 1097m, 1076m, 1029vs, 1004m, 977m, 849w, 734m, 661w, 628w, 574w, 534w, 523w, 481w cm^{-1}; ^{19}F NMR ϕ −53.1 [$(CF_3)_2N$, d], $J[CF_3)_2N-CF] = 16.95$ Hz, −59.2 (NCF_2, d), $J(NCF_2-CF) = 7.53$ Hz, −82.5 (CF, m), −74.9 (CF_3, t), $J(CF-CH_2) = 8.0$ Hz; ^{1}H NMR δ 4.5 (CH_2, q); CI MS [*m/e* (species) intensity] (observed isotopic ratios were correct): 481 ($M^+ + 1$) 0.6, 407 ($M^+ - ClF_2$) 3.1, 381 ($M^+ - OCH_2CF_3$) 0.8, 347 ($M^+ + 1 - OCH_2CF_3 - Cl$) 7.4, 327 ($M^+ - OCH_2CF_3 - ClF$) 60.1, 295 ($M^+ - 2CF_3CH_2 - F$) 16.1, 274 [$CF_2NC(OCHCF_3)_2{}^+$] 62.8, 229 [$CF(OCH_2CF_3)_2{}^+$] 70.0. Analysis: Calcd. for $C_8ClF_{15}H_4N_2O_2$: C, 20.00; H, 0.83; F, 59.38; Cl, 7.29%. Found: C, 20.42; H, 0.95; F, 58.60; Cl, 8.95%.

Characterization of $(CF_3)_2NCF_2N(Cl)CF_2OCH(CF_3)_2$ *(9)*

Having passed through a trap cooled to −10 °C, this product was isolated in 80% yield in a trap cooled to −35 °C. Spectral data obtained were: IR (gas); 3002vw, 1366s, 1353vs, 1305vs, 1255vs, 1220vs, 1197s, 1164m, 1118s, 1098m, 1028vs, 1005m, 982m, 940w, 735m, 716w, 694w cm^{-1}; ^{19}F NMR ϕ −52.9 [$(CF_3)_2N$, m], −58.9 (NCF_2N, m), −73.4 (NCF_2O, m), −73.5 [$(CF_3)_2C$, m]; ^{1}H NMR δ 4.8 (CH, m); CI MS [*m/e* (species) intensity] (correct isotopic ratios were observed): 429 ($M^+ - HF_2$) 17.2, 410 ($M^+ - HF_2 - F$) 17.1, 395 ($M^+ - ClF_2$) 37.7, 365 ($M^+ + 1 - CF_3 - Cl$) 7.0, 344 ($M^+ - CF_3 - HCl - F$) 87.4, 282 [$M^+ + 1 - Cl - (CF_3)_2N$] 100, 217 [$CF_3OCH(CF_3)_2{}^+$] 32.4. Analysis: Calcd. for $C_7ClF_{16}H_1N_2O$: C, 17.95; H, 0.21; F, 64.95; Cl, 7.48%. Found: C, 18.18; H, 0.22; F, 64.2; Cl, 8.28%.

Characterization of $(CF_3)_2NCF_2N(Cl)CF(OCH(CF_3)_2)_2$ *(10)*

This product was found in a trap cooled to −30 °C in 79% yield. Spectral data obtained were: IR (liquid): 2996vw, 1364vs, 1299s, 1208vs, 1113s, 990s, 930w, 903s, 891s, 853vw, 844w, 813w, 787w, 761m, 745m, 731m, 715s, 692s, 636w, 539s cm^{-1}; ^{19}F NMR ϕ -54.4 [$(CF_3)_2N$, t], $J[(CF_3)_2N-CF_2] = 13.18$ Hz, -67.9 (CF_2, q), -73.1 (CF, m), -73.3 [$(CF_3)_2C$, m]; ^{1}H NMR δ 4.69 (CH, spt), $J[(CF_3)_2C-H] = 6.00$ Hz; CI MS [m/e (species) intensity] (observed isotopic ratios were correct): 558 [$(CF_3)_2NCF_2N{=}C(OCH(CF_3)_2)_2^+ + CH_3-F$] 7.0, 492 ($M^+ - CF_3 - Cl - HF$) 4.6, 476 ($M^+ - 2CF_3 - 2H$) 4.2, 429 [$CF_2NCF(OCH(CF_3)_2^+$] 6.8, 410 [$CFNCF(OCH(CF_3)_2)_2^+$] 100, 365 [$CF(OCH(CF_3)_2)_2^+$] 17.4, 262 [$CF_2NCFOCH(CF_3)_2^+$] 24.0. Analysis: Calcd. for $C_{10}ClF_{21}H_2N_2O_2$: C, 19.48; H, 0.33; F, 64.77%. Found: C, 20.00; H, 0.48; F, 61.35%.

Characterization of $(CF_3)_2NCF_2^AN(Cl)CF_2^BOCCH_3(CF_3)_2$ *(11)*

The product was isolated in a -15 °C trap in 60% yield having passed through a trap cooled to 0 °C. Spectral data obtained were: IR (gas): 1358vs, 1328vs, 1244vs, 1214s, 1195s, 1157s, 1121s, 1096s, 1035m, 994s, 970m, 910m, 848m, 751m, 733s, 703m, 534w, 522w, 481m cm^{-1}; ^{19}F NMR ϕ -54.6 [$(CF_3)_2N$, t], $J(CF_3)_2N-A] = 12.24$ Hz, -69.8 (A, m), -54.0 (B, m), -78.5 (CF_3C, m); ^{1}H NMR δ 1.89 (CH_3, hpt), $J(CF_3C-CH_3) = 1.88$ Hz; CI MS [m/e (species) intensity] (observed isotopic ratios were correct): 429 ($M^+ + 1 - ClF$) 0.9, 409 ($M^+ - ClF_2$) 9.0, 358 [$(CF_3)_2NCF_2NCFOC(CH_2)CF_3^+$] 5.9, 342 ($M^+ - 2CF_3$) 1.9, 296 [$(CF_3)_2CCH_3OCF_2NCF_2^+ + 1$] 3.9, 276 [$(CF_3)_2CCH_3OCF_2NCF^+$] 66.3, 247 [$(CF_3)_2NCF_2NCF^+$] 9.1, 231 [$(CF_3)_2CH_3COCF_2^+$] 10.4. Analysis: Calcd. for $C_8ClH_3F_{16}N_2O$: C, 19.92; H, 0.62; F, 63.07%. Found: C, 20.24; H, 0.81; F, 61.1%.

Preparation of $F^AF^BNCClF^CCF^DF^ENCl_2$ *(15)*

Into an evacuated 75 ml stainless steel cylinder equipped with a Whitey valve, were condensed 10 mmol of $F_2NCClFCN$ and 25 mmol of ClF at -196 °C. The reaction mixture was allowed to warm slowly to room temperature and was kept at room temperature for 12 h. Following low-temperature trap-to-trap distillation, the product **15** was found in 95% yield as a pale yellow liquid in the trap cooled to -78 °C. Spectral data obtained were: ^{19}F NMR ϕ $+35.6$ (A, m), -129.8 (B, m), -104.3 (C, m), -89.5 (E, m), -93.7 (F, m), $J(A-B) = 644$ Hz, $J(A-C) = 8.5$ Hz, $J(A-D) = 1.2$ Hz, $J(A-E) = 7.7$ Hz, $J(B-C) = 8.4$ Hz, $J(B-D) = 24.0$ Hz, $J(B-E) = 7.2$ Hz, $J(C-D) = 7.7$ Hz, $J(C-E) = 7.9$ Hz, $J(D-E) = 18.6$ Hz; CI MS [m/e (species) intensity] (correct isotopic ratios were observed): 252 (M^+) 0.7, 233 ($M^+ - F$) 0.5, 199 ($M^+ + 1 - ClF$) 11.3, 146 ($C_2F_2NCl_2^+$) 100, 134 ($CF_2NCl_2^+$) 4.3. Analysis: Calcd. for $C_2Cl_3F_5N_2$: C, 9.47; N, 11.07%. Found; C, 9.59; N, 11.22%.

Preparation of $(F^AF^BNCClFCF^CF^DN{=})_2$ *(17)*

A 500 ml quartz vessel equipped with a Teflon stopcock was evacuated, and 1.5 mmol of $F_2NCClFCF_2NCl_2$ was added. Following photolysis using 3000 Å UV lamps for 2 h, the product **17** was obtained as a light yellow liquid in a trap cooled to -78 °C (96% yield). Spectral data obtained were:

IR (gas): 1229vs, 1163vs, 1101m, 985s, 951s, 915vs, 779w, 726m, 695w, 664m, 590vw, 561w, 503w cm^{-1}; ^{19}F NMR ϕ +34.0 (A, m), +28.5 (B, m), J(A−B) = 640 Hz, −115.2 (CFCl, m), −103.9 (CF^{C}F^{D}, m), J(C−D) = 8.2 Hz; CI MS [m/e (species) intensity] (correct isotopic ratios were observed): 365 (M^+-1) 0.1, 345 (M^+-F) 0.3, 311 ($M^++1-ClF$) 1.3, 291 (M^+-ClF_2) 1.2, 275 (M^+-Cl_2F) 2.0. Analysis: Calcd. for $C_4Cl_2F_{10}N_4$: C, 13.15; N, 15.34%. Found: C, 13.30; N, 15.37%.

Preparation of $F_2NCF_2^{A}CF_2^{B}N(Cl)CF_2^{C}CCl_2F^{D}$ (18)

When 12 mmol of $F_2NCF_2CF_2NCl_2$ and 13 mmol of CF_2CClF were condensed into a 75 ml stainless steel vessel equipped with a Whitey valve, and heated at 65–70 °C for 12 h, the product $F_2NCF_2CF_2N(Cl)CF_2CCl_2F$ was obtained in ≈40% yield. It was isolated in a trap cooled to −78 °C by low-temperature trap-to-trap distillation. Spectral data obtained were: IR (gas): 1775vw, 1240vs, b, 1152vs, b, 1090vs, 1067s, 971vs, 926vs, 903vs, 854m, 797s, 747vs, 659m, 642m, 598m, 542w, 483vw, 467vw cm^{-1}; ^{19}F NMR ϕ +18.59 (NF$_2$, m), −70.0 (D, m), −89.1 (B, C, m), −112 (A, b, m); CI MS [m/e (species) intensity] (correct isotopic ratios were observed): 333 (M^+-F) 0.4, 318 (M^++1-Cl) 0.4, 301 (M^++1-NF_2) 25.8, 279 ($C_4Cl_2F_7N_2^+$) 63.8, 263 ($C_4ClF_8N_2^+$) 99.6, 151 ($CF_2CFCl_2^+$) 40.7, 103 ($CF_2NF_2^++1$) 88.3. Analysis: Calcd. for $C_4Cl_3F_9N_2$: C, 13.64; N, 7.95%. Found: C, 13.86; N, 7.82%.

Preparation of $F_2NCF_2^{A}CF_2^{B}N{=}CF_2$ (19)

When 10 mmol of $F_2NCF_2CF_2N(Cl)CF_2CCl_2F$ was condensed into a 250 ml quartz vessel and irradiated (3000 Å) for 5 h, **19** was obtained in essentially quantitative yield by low-temperature distillation in a trap cooled to −78 °C. Spectral data obtained were: IR (gas): 1805, 1801 (ν C=N) vs, 1316vs, 1250vs, 1171vs, 1088m, 988m, 974s, 928vs, 887m, 831vw, 979w, 718w, 639w, 598w, 542w cm^{-1}; ^{19}F NMR ϕ +18.13 (NF$_2$, b), −118.9, −91.7 (A, B, m, b), −41.87 (=CF, m), −25.8 (−CF, m), J(CF−CF) = 220 Hz; CI MS [m/e (species) intensity]: 217 (M^++1) 28.1, 197 (M^+-F) 22.6, 164 (M^+-NF_2) 50.8, 114 ($CF_2N{=}CF_2^+$) 100, 100 ($C_2F_4^+$) 30, 64 (CF_2N^+) 1.7.

Preparation of $F_2NCF_2^{A}CF_2^{B}N(Cl)CF_3^{C}$ (20)

$F_2NCF_2CF_2N{=}CF_2$ (10 mmol) and ClF (12 mmol) were condensed at −196 °C into an evacuated 75 ml stainless steel vessel equipped with a Whitey valve. The reaction mixture was allowed to warm slowly to room temperature and kept at that temperature for 12 h. The product was purified by low-temperature trap-to-trap distillation and was found in the trap cooled to −78 °C. Spectral data obtained were: IR (gas): 1332m, 1289vs, 1246vs, 1213vs, 1188vs, 1179vs, 1080m, 1051w, 1041w, 1030w, 1022w, 1014vw, 976s, 934s, 880m, 846vs, 791m, 718m, 629w, 610w, 572w cm^{-1}; ^{19}F NMR ϕ +18.5 (NF$_2$, b), −59.6 (CF$_3$, t, t), J(B−C) = 13.4 Hz, J(A−C) = 3.7 Hz, −94.6 (B, q, t), J(C−B) = 13.4 Hz, J(NF$_2$−B) = 3.5 Hz, −114.0 (A, q, b) J(NF$_2$−A) < 1 Hz; CI MS [m/e (species) intensity] (correct isotopic ratios were observed): 252 ($M^+ + 1 - F$) 1.2, 251 ($M^+ - F$) 4.6, 217 ($F_2NCF_2CF_2NCF_2^+ + 1$) 44.9, 165 ($CF_2CF_2NCF_2^+ + 1$) 34.6, 164 ($CF_2CF_2NCF_2^+$) 38.8, 145 ($CF_2CF_2NCF^+$) 27.6, 101 ($C_2F_4^+ + 1$) 51.2, 69 (CF_3^+) 80. Analysis: Calcd. for $C_3F_9ClN_2$: C, 13.33; N, 10.37%. Found: C, 13.42; N, 10.29%.

Preparation of $F_2NCF_2^ACF_2^BN(CF_3)N{=}CCl_2$ *(21)*

Into a 200 ml quartz vessel were combined 5 mmol of $F_2NCF_2CF_2N(Cl)CF_3$ and 8 mmol of ClCN. The mixture was irradiated. for 11 h at 3000 Å. The product was isolated in a trap cooled to −20 °C by low-temperature distillation. Spectral data obtained were: IR (gas): 1585vs (ν N=C), 1343m, 1289vs, 1246vs, 1217vs, 1196vs, 1178vs, 1083w, 992vs, 933m, 891m, 869w, 848m, 777m, 737m, 697m, 677vw, 644vw, 618vw, 606vw, 482m cm^{-1}; ^{19}F NMR ϕ +18.3 (NF_2, b), −59.8 (CF_3, t, t), $J(CF_3,B) = 12.2$ Hz, $J(CF_3,A) = 3.7$ Hz, −99.7 (B, m), −115.8 (A, m). Analysis: Calcd. for $C_4F_9Cl_2N_3$: C, 14.50; N, 15.71%. Found: C, 14.61; N, 12.69%.

Preparation of $F_2NCF_2^ACF_2^BN(CF_3)N{=}C(Cl)CF_2^CNF_2$ *(22)*

To a 200 ml quartz vessel were added 5 mmol of $NF_2CF_2CF_2N(Cl)CF_3$ and 8 mmol of F_2NCF_2CN. The mixture was photolyzed at 3000 Å for 11 h. The product was isolated in a trap cooled to −20 °C by low-temperature distillation. Spectral data obtained were: IR (gas): 1631m, 1343m, 1284vs, 1250vs, 1230vs, 1193vs, 1177s, 1165s, 1139m, 1084w, 1024m, 979m, 935s, 894m, 866w, 850w, 790w, 769w, 731vw, 699vw cm^{-1}; ^{19}F NMR ϕ +19.7 (NF_2, s), +17.5 (NF_2, s), −59.4 (CF_3, t), $J(CF_3,B) = 18.0$ Hz, −100.0 (B), −103.3 (A), −115.9 (C). Analysis: Calcd. for $C_5F_{13}ClN_4$: C, 15.08; N, 14.07%. Found: C, 15.32; N, 13.88%.

Preparation of $F_2NCF_2CF_2N(CF_3)N(Cl)CClFCF_2NF_2$ *(23)*

At −196 °C, 5 mmol of $F_2NCF_2CF_2N(CF_3)N{=}CClCF_2NF_2$ and 8 mmol of ClF were combined in a 75 ml stainless steel vessel. The mixture was allowed to warm slowly to room temperature, and to remain at that temperature for 24 h. An 80% yield of $F_2NCF_2CF_2N(CF_3)N(Cl)CClFCF_2NF_2$ was isolated in a trap cooled to −45 °C by low-temperature trap-to-trap distillation. Spectral data obtained were: IR (gas): 1303vs, 1254s, 1164s, 1075m, 1029m, 987w, 948m, 866w, 815w, 772m, 729m cm^{-1}; ^{19}F NMR ϕ +22.1, +21.66, +20.16 (NF_2, m), −55.9, −56.7, −58.8 (CF_3, m), −92.8, −97.4, −101.8, −110.8, −112.2, −112.3, −113.6, −115.0 (CF_2, CF, m); CI MS [m/e (species) intensity] (correct isotopic ratios were observed): 452 (M^+) 1.7, 417 ($M^+ - Cl$) 4.3, 383 ($M^+ - CF_3$) 0.7, 363 ($M^+ + 1 - NF_2 - 2F$) 22.9, 331 ($M^+ - NF_2 - CF_3$) 4.9, 330 [$F_2NCF_2CF_2N(CF_3)NCFCF_2^+$] 62.0, 280 [$CF_2CFN(CF_3)N(Cl)CFCl^+ + 1$] 14.2, 278 [$CF_2CF_2N(CF_3)NCFCF_2^+$] 4.6, 114 ($C_2F_4N^+$) 15.1, 100 ($C_2F_4^+$) 70.0, 84 ($CF_3N^+ + 1$) 10.6, 83 ($CF_3N^+$) 1.5, 69 ($CF_3^+$) 100.

*Preparation of $F_2NCF_2CF_2N(CF_3)N{=}CFCF_2NF_2$ (**24**)*

Compound **23** (4 mmol) was transferred into a 200 ml quartz vessel at −196 °C, allowed to warm to room temperature, and photolyzed at 3000 Å for 5 h. The product was collected in 90% yield in a trap cooled to −60 °C. Spectral data obtained were: IR (gas): 1721m, 1347m, 1300vs, 1231vs, 1225vs, 1199s, 1177s, 1086w, 978m, 938m, 908w, 879vw, 795vw, 742w, 656vw, 511vw cm^{-1}; ^{19}F NMR ϕ +21.5, +18.5 (NF_2, m), −43.8 (CF, m, b), −58.7 (CF_3, m), −96.5 (CF_2, m), −105.3 (CF_2, m), −114.6 (CF_2, m); CI MS [*m/e* (species) intensity]: 383 ($M^+ + 1$) 1.6, 363 ($M^+ - F$) 1.0, 311 ($M^+ - NF_2 - F$) 4.5, 280 ($M^+ - CF_2NF_2$) 16.0, 261 ($M^+ - CF_2NF_2 - F$) 5.4, 114 ($C_2F_4N^+$) 10.0, 109 ($CF_2N_2CF^+$) 13.2, 102 ($CF_2NF_2^+$) 0.7, 84 ($CF_3N^+ + 1$) 8.6, 69 (CF_3^+) 82.9. Analysis: Calcd. for $C_5F_{14}N_4$: C, 15.71; N, 14.66%. Found: C, 15.81; N, 14.66%.

*Preparation of $F_2NCF_2CF_2N(Cl)N(CF_3)CF_2CF_2NF_2$ (**25**)*

When 3.5 mmol of compound **24** and 5 mmol of ClF were combined into a 75 ml stainless steel vessel, and allowed to warm slowly to room temperature and stand at that temperature for 24 h, the product (**25**) was formed in quantitative yield. It was isolated by low-temperature trap-to-trap distillation and collected in a trap cooled to −30 °C. Spectral data obtained were: IR (gas): 1315m, 1253s, 1201w, 1175m, 1087w, 1061w, 1029s, 974w, 934m, 898w, 859w, 736m; ^{19}F NMR ϕ +19.4, +18.3, +17.7 (NF_2, b), −57.2, −59.5 (CF_3, m), −95.3 (CF_2CF_2, m), −114.7 (CF_2CF_2, m); CI MS [*m/e* (species) intensity] (correct isotopic ratios were observed): 451 ($M^+ + CH_3$) 3.3, 418 ($M^+ + 1 - F$) 0.8, 383 ($M^+ + 1 - ClF$) 1.6, 363 ($M^+ - ClF_2$) 19.7, 311 ($M^+ - ClF_2 - NF_2$) 2.3, 280 [$F_2NCF_2CF_2NN(CF_3)CF^+$] 10.4, 114 ($C_2F_4N^+$) 18, 100 ($C_2F_4^+$) 8.7, 69 (CF_3^+) 100. Analysis: Calcd. for $C_5F_{15}N_4Cl$: C, 13.76; N, 12.84%. Found: C, 13.67; N, 12.70%.

*Preparation of $[F_2NCF_2CF_2N(CF_3)N(CF_2CF_2NF_2)]_2$ (**26**)*

Compound **25** was transferred to a 50 ml quartz vessel and photolyzed at 3000 Å for 4 h. The product (**26**) was obtained in 70% yield as a thick, colorless, non-volatile liquid. Spectral data obtained were: IR (liquid): 1240s, b, 1156s, b, 1063s, b, 1019s, 984s, 969s, 942s, 889s, 862s, 622m, 603m, 540m cm^{-1}; ^{19}F NMR ϕ +19.3 (NF_2, m, b), −57.1 (CF_3, m), −89.8 (CF_2, 8F, m), −114.2 (CF_2, 8F, m); CI MS [*m/e* (species) intensity]: 611 [$CF_2CFNN(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF_2CF_2^+ + 1$] 0.8, 561 [$CF_2CFNN(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF_2^+ + 1$] 2.0, 541 [$CF_2CFNN(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF^+$] 2.0, 508 [$CF_2CFNN(CF_2CF_2NF_2)N(CF_2CF_2)N(CF_3)CF_2^+$] 4.0, 491 [$CFNN(CF_2CF_2NF_2)N(CF_2CF_2NF_2)N(CF_3)CF^+$] 7.8, 401 ($M^+/2$) 3.2, 382 ($M^+/2 - F$) 50.4, 330 ($M^+/2 - NF_2 - F$) 100, 299 ($M^+/2 - CF_2NF_2$) 5.9, 280 ($M^+/2 - CF_2NF_2 - F$) 60.4, 197 ($F_2NCF_2CF_2NCF^+$) 96, 166 ($F_2NCF_2CF_2N^+$) 5.0, 102 ($F_2NCF_2CF_2^+$) 9.3. Analysis: Calcd. for $C_{10}F_{30}N_8$: C, 14.96; N, 13.96%. Found: C, 14.58; N, 13.78%.

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