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Some Highly Fluorinated Acyclic, Cyclic, and Polycyclic Derivatives of $Cl_2NCF_2CF_2NCl_2$ and $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$

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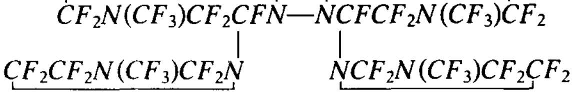
ABSTRACT

When $Cl_2NCF_2CF_2NCl_2$ *is heated with* $CF_2{=}CFX$ (X = Cl, F) $ClXCFCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF$ (X = Cl, **2**; F, **3**) *is formed. Mercury extracts chlorine fluoride from* **2** *and* **3** *to form new polyfluorobisazomethines,* $ClXCFCF_2N{=}CFCF{=}NCF_2CXClF$ (X = Cl, **4**; F, **5**). *Photolysis of the product obtained from* $CCl_2{=}NCCl_2CCl_2N{=}CCl_2$ *with ClF,* $CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl$ (**6**) *gives another bisazomethine,* $CF_2ClN{=}CFCF{=}NCF_2Cl$ (**7**) *with concomitant loss of* Cl_2. *At 25°C, in the presence of CsF,* **4** *and* **5** *are cyclized to give* $ClXCFC{=}NCF_2CF_2NCF_2CXClF$ (X = Cl, **8**; F, **9**), *and* **7** *forms a bicyclic derivative at 100°C,* $CF_2CF_2N(CF_3)CF_2N{-}C{=}NCF_2N(CF_3)CF_2$ (**1**). *Addition of chlorine fluoride to* **8** *and to* **1** *produces* $FCl_2CCFN(Cl)CF_2CF_2NCF_2CCl_2F$ (**10**) *and* $CF_2CF_2N(CF_3)CF_2N{-}CFN(Cl)CF_2N(CF_3)CF_2$ (**14**), *respectively. Photolysis of* **10** *results in the loss of* $CFCl_3$ *to form* $FC{=}NCF_2CF_2NCF_2CCl_2F$ (**11**), *and* **14** *loses* Cl_2 *and dimerizes to the hydrazine*



$$\begin{array}{cc} CF_2N(CF_3)CF_2CFN & {-}NCFCF_2N(CF_3)CF_2 \\ | & | \\ CF_2CF_2N(CF_3)CF_2N & NCF_2N(CF_3)CF_2CF_2 \end{array}$$

(**15**). *The further addition of ClF to* **11** *gives rise to* $CF_2CF_2N(Cl)CF_2NCF_2CCl_2F$ (**12**) *which when photolyzed at 3000 Å forms a second cyclic hydrazine,* $CF_2N(CF_2CCl_2F)CF_2CF_2N{-}NCF_2CF_2N(CF_2CCl_2F)CF_2$ (**13**).

INTRODUCTION

The chemistry of the nitrogen—halogen bond has long attracted interest because of the ease with which reactions occur and the range of compounds of varying properties that can be prepared. These compounds in turn are often viable precursors to stable high-nitrogen and high-fluorine materials.

We and others [1,2] have taken advantage of this high reactivity to insert perfluoroalkenes and polyfluoroalkenes into the nitrogen—chlorine bond(s) of R_fNCl_2 to prepare either secondary polyfluoroalkyl- or perfluoroalkylchloroamines or tertiary polyfluoroalkyl- or perfluoroalkylamines.

$$R_fNCl_2 + CF_2{=}CFX \xrightarrow{65\text{–}70^\circ C} R_fN(CF_2CFClX)Cl \quad (1)$$

$$X = Cl, F$$

$$R_fNCl_2 + 2\,CF_2{=}CFX \xrightarrow{95\text{–}100^\circ C} R_fN(CF_2CFClX)_2 \quad (2)$$

Photolysis of the N-chloroamines provides a powerful route to azaalkenes, e.g., $R_fN(CF_2CFClX)Cl \xrightarrow{h\nu} R_2N{=}CF_2 + CFXCl_2$. In earlier reports [1, 2] we have enumerated further reactions of the N,N-dichlorodiamines. Olefins insert with equal ease into the N—X bond of $CF_2{=}NX$ (X = Cl, Br) [3, 4].

Nitriles [2] can be inserted into $R_fR_f'NCl$ to form precursors to polyfluoroalkyl and perfluoroalkyl tetrazanes as well as other high-nitrogen compounds.

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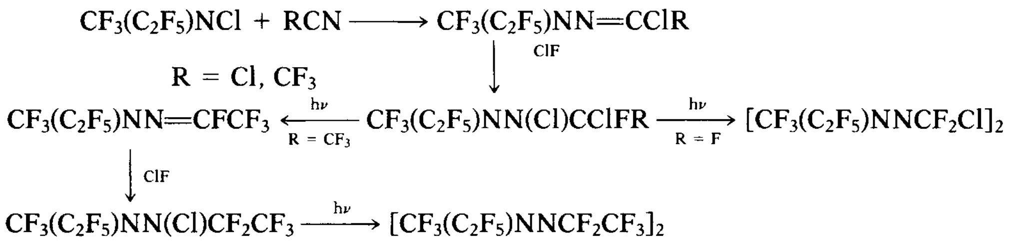


$$\begin{tikzcd}
\mathrm{CF_3(C_2F_5)NCl + RCN} \arrow[r] & \mathrm{CF_3(C_2F_5)NN{=}CClR} \arrow[d, "\mathrm{ClF}"] & \\
\mathrm{CF_3(C_2F_5)NN{=}CFCF_3} \arrow[d, "\mathrm{ClF}"] & \mathrm{CF_3(C_2F_5)NN(Cl)CClFR} \arrow[l, "h\nu"', "\mathrm{R = CF_3}"] \arrow[r, "h\nu", "\mathrm{R = F}"'] & \mathrm{[CF_3(C_2F_5)NNCF_2Cl]_2} \\
\mathrm{CF_3(C_2F_5)NN(Cl)CF_2CF_3} \arrow[r, "h\nu"] & \mathrm{[CF_3(C_2F_5)NNCF_2CF_3]_2} &
\end{tikzcd}$$

$\mathrm{R = Cl, CF_3}$

Fluoroolefins that contain terminal double bonds, and perfluoro-α, ω-bisazomethines are readily isomerized in the presence of fluoride ions [5, 6]. Similar behavior is observed with fluoride ion for compounds such as $(R_f)_2NN{=}CClR_f'$ (R_f' = Cl or *F*-alkyl) where fluorination and dimerization occur readily [2, 7]. Totally chlorinated compounds such as $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$, when heated with NaF/TMSO, or with HF followed by CsF/CH$_3$CN, give $CF_2N(CF_3)CF_2CF_2N{-}C{=}NCF_2N(CF_3)CF_2$, **1**, [8] or $F_2CC({=}NCF_3)N(CF_3)CF(CF{=}NCF_3)N(CF_3)$ + **1** [9], respectively.

In this report we have extended our study of the reactivity of the nitrogen—chlorine bond by comparing the reaction chemistry of $Cl_2NCF_2CF_2NCl_2$ [10] with that of the R_fNCl_2 compounds. For instance, we find that in contrast to the reactions of R_fNCl_2 after the symmetrical insertion of the first two olefin molecules, it is very difficult to introduce additional olefin molecules into the two remaining N—Cl bonds of $R_fN(Cl)CF_2CF_2N(Cl)R_f$. Utilizing $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ as the precursor, we have also compared the reaction behavior of $ClCF_2N{=}CFCF{=}NCF_2Cl$ with $CFCl_2CF_2N{=}CFCF{=}NCF_2CFCl_2$ (obtained from $Cl_2NCF_2CF_2NCl_2$) under identical conditions and find remarkable differences.

RESULTS AND DISCUSSION

With a single exception [11], until our recent report [1] there has been no evidence for studies involving insertion reactions of fluoro-olefins with N,N-dichloroperhaloalkylamines to form secondary or tertiary poly- or perfluoroalkylamines. As is indicated in Equations (1) and (2), the formation of the product secondary or tertiary amines is temperature-dependent. This was amply demonstrated when reaction (1) was carried out at 65–70°C with a large excess of olefin and only the secondary amine was obtained. By using either a 1 : 1 (dichloroamine : olefin) stoichiometry or 1 : ≥2 at 95–100°C, the sole product was the tertiary amine with unreacted dichloroamine recovered in the former case. Although the mechanism is believed to be free radical, only a single isomer is obtained from the reactions between R_fNCl_2 and unsymmetric chlorofluoroolefins [1, 12].

Two moles of chlorotrifluoroethene or tetrafluoroethene are readily inserted symmetrically into two nitrogen-chlorine bonds of 1 mole of $Cl_2NCF_2CF_2NCl_2$. At 65–70°C, even in the presence of the excess olefin, the product is invariably formed from 1 mole of amine and 2 moles of olefin.

$$\mathrm{Cl_2NCF_2CF_2NCl_2 + 2CF_2{=}CFX} \xrightarrow[\text{10–12 h}]{\text{65–70°C}}$$

$$\mathrm{ClXCFCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF}$$

$$\mathrm{X = Cl,\ \mathbf{2};\ F,\ \mathbf{3}}$$

As is the case with the mono(dichloroamines), only a single isomer is obtained with $CF_2{=}CFCl$. The presence of a major fragment corresponding to $CFCl_2^+$ in the mass spectrum in addition to appropriate ^{19}F nuclear magnetic resonance (NMR) resonance bands support the presence of **2** only. When the reactions were performed at 95–100°C, very complicated mixtures of products were obtained. These reactions at higher temperature were not studied further.

When compound **2** or **3** is stirred with elemental mercury for several hours the remaining N—Cl bonds are broken and 2 moles of ClF are removed.

$$\mathbf{2}\ \text{or}\ \mathbf{3} + 2\ \mathrm{Hg} \xrightarrow[\text{10–12 h}]{\text{25°C}}$$

$$\mathrm{ClXCFCF_2N{=}CFCF{=}NCF_2CXClF + 2\ HgClF}$$

$$\mathrm{X = Cl,\ \mathbf{4}\ (60\%);\ F,\ \mathbf{5}\ (50\%)}$$

In the infrared (IR) spectra of **4** and **5**, absorption bands at 1736 and 1744 cm^{-1} are assigned to $\nu_{C=N}$, respectively. In their mass spectra, major fragments corresponding to $CXClF^+$, as well as the ^{19}F NMR spectral data, support the loss of fluorine from the $>NCF_2CF_2N<$ portion of the molecules. Another new polyfluoro-α,ω-bisazomethine was obtained when the product formed from the reaction of chlorine fluoride with $CCl_2{=}NCCl_2CCl_2N{=}CCl_2$ was photolyzed,

$$\mathrm{CCl_2{=}NCCl_2CCl_2N{=}CCl_2 + ClF} \rightarrow$$

$$\mathrm{CF_2Cl\underset{\displaystyle Cl}{N}CFClCFCl\underset{\displaystyle Cl}{N}CF_2Cl}$$

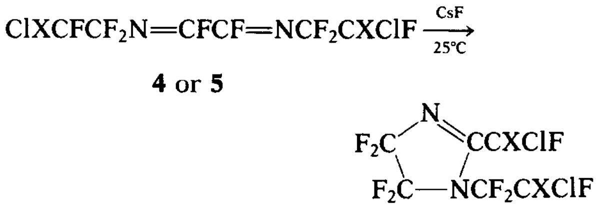
6

$$\mathbf{6} \xrightarrow[-2Cl_2]{h\nu} \mathrm{CF_2ClN{=}CFCF{=}NCF_2Cl}$$

7

On standing, **6** loses Cl_2 slowly to give **7**. The rate of dechlorination is enhanced by photolysis. For **7**, the absorption band assigned to $\nu_{C=N}$ in the IR spectrum is observed at 1734 cm^{-1}. Here also the base peak in the mass spectrum is assigned to CF_2Cl^+. Typically, the chemical shifts in the ^{19}F NMR spectra of the methine fluorine atoms **4**, **5**, and **7** are found in the region of ϕ −22 to −26. In $CF_3N{=}CFCF{=}NCF_3$, the resonance band at ϕ −25 in the ^{19}F NMR spectrum is assigned to CF [6].

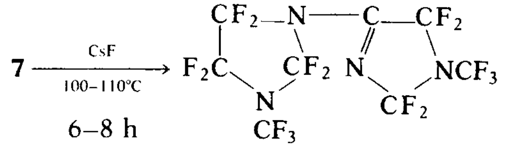
At this stage, it became interesting to observe the behavior of **4**, **5**, and **7** when each was reacted with CsF at 25°C. In the case of **4** and **5**, the respective heterocyclic isomers are formed



4 or **5**

X = Cl, **8** (75%); F, **9**, (70%)

while with **7**, CsF gives rise to a stable bicyclic derivative that had been synthesized earlier



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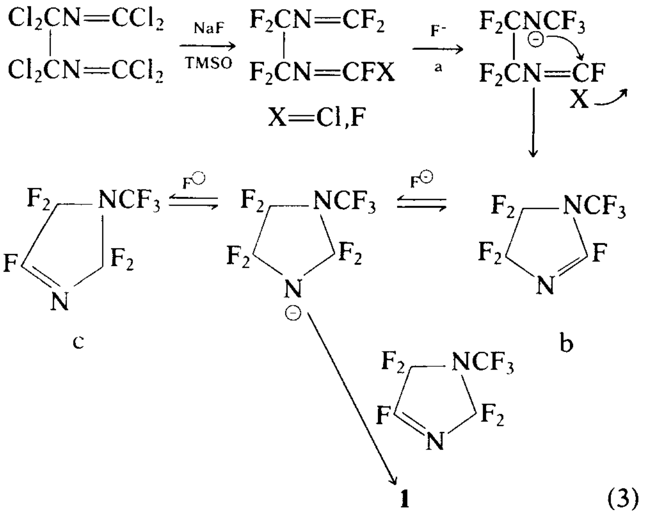
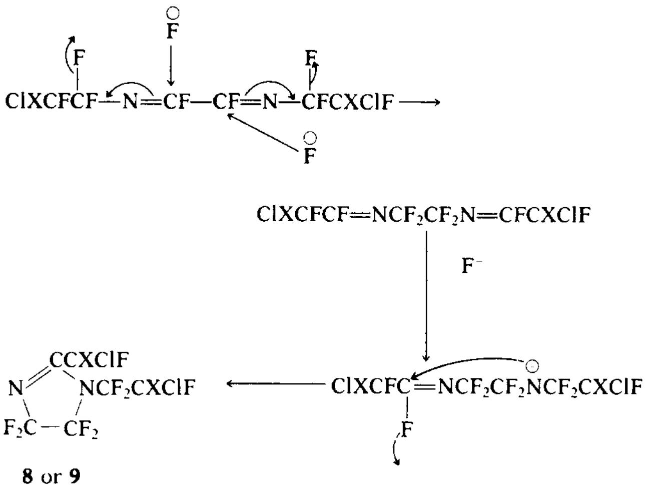
by heating a mixture of $CCl_2N{=}CCl_2CCl_2N{=}CCl_2$ and NaF in tetramethylene sulfone [8],



(3)

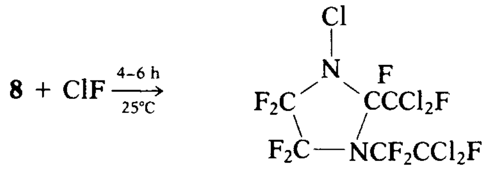
The cyclization of **4** or **5** must occur in a manner similar to step (3a) above, e.g.,



8 or **9**

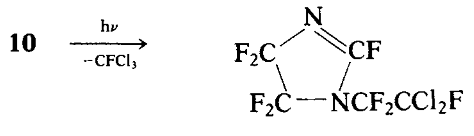
This is a particularly interesting reaction since normally in the presence of fluoride ion bisazomethines are isomerized very readily to carbodiimides or perfluorodiazadienes [6], while just the reverse isomerization must have occurred prior to cyclization in the case of **4** or **5**. The only difference between compounds **4** and **5**, and compound **7** is the alkyl substituent at nitrogen, CF_2Y (Y = CCl_2F in **4**; $CClF_2$ in **5**; and Cl in **7**). This is apparently the key to the products obtained. The bisazomethine **7** isomerizes first to the α, ω-bisazomethine and then the reaction with F^- proceeds as in Equation (3). The option to form the two isomers (3b) and (3c) via a fluoride ion shift provides a pathway to the bicyclic molecule **1** that is not available for the case where the reactant has a longer-chain alkyl substituent at nitrogen (**4**, **5**). The carbon—nitrogen double bond is observed at 1636, 1652, and 1680 cm^{-1} in the stable heterocycles **8**, **9**, and **1**, respectively.

Advantage was taken of the susceptibility of the >C=N— bond in **8** to the addition of chlorine fluoride to form a new cyclic chloroamine



10 (80%)

which when photolyzed loses $CFCl_3$



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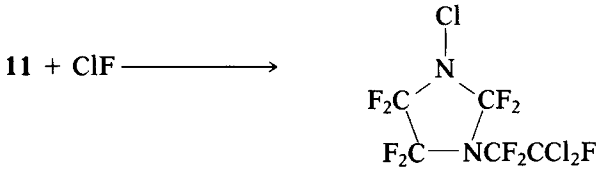
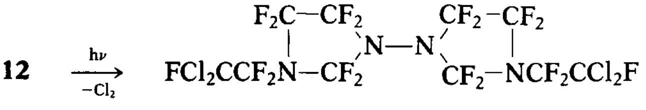
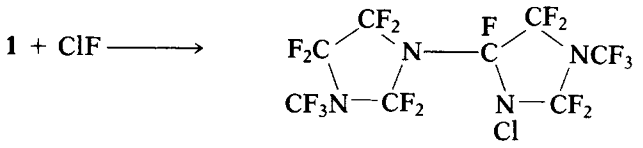
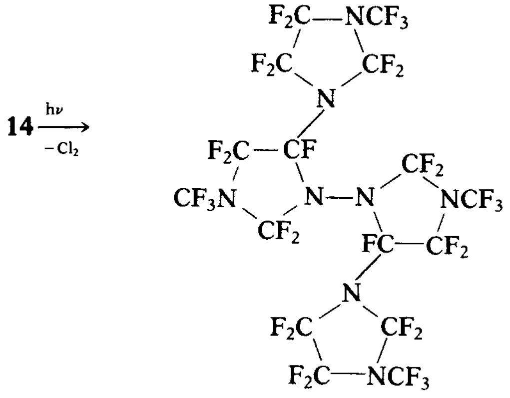
This behavior is not surprising since we had observed the analogous loss of $CFCl_3$ when $R_fN(Cl)CF_2CFCl_2$ was photolyzed to form $R_fN{=}CF_2$ [1]. The $\nu_{C=N}$ band in **11** is observed at 1719 cm^{-1}. The addition of another mole of chlorine fluoride to **11** gave **12** which when photolyzed formed a new bicyclic hydrazine **13** with the concomitant loss of Cl_2


12 (80%)


13

A more highly substituted, yet stable, cyclic hydrazine **15** was obtained when **1** was reacted with ClF to form the chloroamine **14** which was then photolyzed. Both **14** and **15** are involatile liquids of marginal solubility in ordinary solvents.


14 (80%)


15 (20%)

The ^{19}F NMR spectra of many of these new compounds are highly complex and in some cases we have not been entirely successful in establishing all of the J values, particularly in cases where the molecule contains multiple chiral centers, e.g., in **6** where there are four such centers. As might be imagined this seemingly straightforward molecule has an extremely complex ^{19}F NMR spectrum.

CONCLUSION

The reactions of $Cl_2NCF_2CF_2NCl_2$ and $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ provide routes to an interesting family of acyclic, cyclic, and bicylic compounds that contain high concentrations of both nitrogen and fluorine. The majority are thermally and hydrolytically stable and may have useful applications where such fluids are needed.

EXPERIMENTAL

Materials

The reagent $Cl_2NCF_2CF_2NCl_2$ was prepared according to the literature [10]. $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ was a gift of Dr. E. Klauke (Bayer AG, Leverkusen, Federal Republic of Germany). Other chemicals were purchased and used as received: chlorine fluoride (Ozark-Mahoning); $CF_2{=}CF_2$ and $CF_2{=}CFCl$ (PCR); $(CN)_2$ (Matheson); and cesium fluoride (American Potash).

General Procedures

Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system fitted with Heise Bourdon tube and Televac thermocouple gauges. Volatile starting materials and products were quantitated by using PVT techniques. Separation and purification of products were realized by using trap-to-trap distillation for volatile compounds. Distillation under dynamic vaccum was required for compounds of low volatility. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform IR spectrometer with a 10-cm gas cell equipped with KBr windows. ^{19}F NMR spectra were measured on a JEOL FX-90Q Fourier transform NMR spectrometer with CCl_3F as reference and $CDCl_3$ as solvent. Mass spectra were obtained with a VG 7070HS mass spectrometer operating at an ionization potential of 17 eV. Appropriate chlorine isotope ratios were obtained in all cases. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Federal Republic of Germany. Photolysis reactions were carried out in quartz reaction vessels at 3000 Å by using a Rayonet photochemical reactor. Theoretical ^{19}F NMR spectra were calculated by using the PMR program (Serena Software).

Reaction of Olefins ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) with $Cl_2NCF_2CF_2NCl_2$

Preparation of $ClXCFCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF$ (X = Cl, **2**; F, **3**). Ten mmol of $Cl_2NCF_2CF_2NCl_2$ and 25 mmol of olefin ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) were condensed at −196°C into a 50-mL thick-walled Pyrex reaction tube. The tube was sealed and heated at 65–70°C for 12–14 h. The product was separated by trap-to-trap distillation.

Properties of $Cl_2CF^ACF_2^BN(Cl)CF_2^CCF_2^DN(Cl)CF_2CFCl_2$ **2.** The compound is involatile. It was obtained as a very light-yellow liquid in ~70%–75% yield. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 392 ($C_6F_8Cl_4N_2^+$) 2.74, 357 ($C_6F_8Cl_3N_2^+$) 8.06, 291 ($C_5F_7Cl_2N_2^+$) 28.2, 196 ($C_3F_4Cl_2N^+$) 36.3, 180 ($C_3F_5ClN^+$) 47.5, 151 ($C_2F_3Cl_2^+$) 79.8, 114 ($C_2F_4N^+$) 100, 101 ($CFCl_2^+$) 94.8; IR (liq): 1256 vs, 1224 vs, 1142 vs, 1090 vs, 1056 s, 954 m, 902 vs, 767 m, 730 s, 679 m, cm^{-1}. ^{19}F NMR: ϕ −70.19 (A, tt), −87.22, −87.33 (C, td), −90.17 (B, dt), J_{A-C} = 8.42 Hz, J_{A-B} = 7.63 Hz, J_{B-C} = 13.5 Hz, J_{C-D} = 2.8 Hz, J_{B-D} = 7.5 Hz. Anal. Calcd. for $C_6F_{10}Cl_6N_2$: C, 14.40, F, 38.0, N, 5.60, Cl, 42.00. Found: C, 14.59, F, 39.1, N, 5.48, Cl, 40.84.

Properties of $ClCF_2^ACF_2^BN(Cl)CF_2^CCF_2^DN(Cl)CF_2CF_2Cl$ **3.** The compound is slightly volatile, moves slowly under dynamic vacuum, and stops in a trap at 0°C. It was obtained as a light-yellow liquid in ~65% yield. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 415 (M^+ + 1 − ClF) 0.57, 341 ($C_6F_9Cl_2N_2^+$) 7.35, 275 ($C_5F_8ClN_2^+$) 26.4, 230 ($C_4F_7ClN^+$) 10.4, 180 ($C_3F_5ClN^+$) 37.96, 164 ($C_3F_6N^+$) 10.25, 135 ($C_2F_4Cl^+$) 100, 85 (CF_2Cl^+) 87.4; IR (liq): 1251 vs, 1170 s, 1150 s, 1107 vs, 1055 s, 974 vs, 793 m, 770 m, 748 ms, cm^{-1}; ^{19}F NMR: ϕ −67.53 (A, tt), −88.72 (C, D, ttt) −92.20 (B, ttt). J_{A-B} = 2.32 Hz, J_{A-C} = 6.84 Hz, J_{B-C} = 13.5 Hz, J_{B-D} = 7.5 Hz; J_{C-D} = 2.8 Hz.

Reactions of $ClXCFCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF$ (X = Cl, F) with Hg

Preparation of $ClXCFCF_2N{=}CFCF{=}NCF_2CXClF$ (X = Cl, **4**; F, **5**). Five mmol of $CFXClCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF$ was condensed onto mercury in a flask fitted with a Teflon stopcock. The contents were stirred for 6–8 h at 25°C. The products obtained were separated by trap-to-trap distillation.

Properties of $Cl_2CF^ACF_2^BN{=}CF^CCF{=}NCF_2CCl_2F$ **4.** This compound was stopped in a trap cooled at −10°C. It was obtained in 60%–65% yield. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 393 (M^+ + 1) 2.20, 373 (M^+ − F) 13.33, 357 (M^+ − Cl) 7.57, 291 ($C_5F_7Cl_2N_2^+$) 28.0, 196 ($C_3F_4Cl_2N^+$) 14.4, 151 ($C_2F_3Cl_2^+$) 100; 101 ($CFCl_2^+$) 71.22; IR (gas): 1768, 1736 s ($\nu_{C=N}$), 1291 w, 1257 s, 1232 ms, 1207 vs, 1173 w, 1153 s, 1087 m, 1029 s, 911 ms, 861 w, 809 w, cm^{-1}; ^{19}F NMR: ϕ −22.82 (C, br t), −74.71 (A, td), −91.79 (B, dd). J_{A-B} = 9.03 Hz, J_{B-C} = 20.0 Hz, J_{A-C} = 6.22 Hz.

Properties of $ClCF_2^ACF_2^BN{=}CF^CCF{=}NCF_2CF_2Cl$ **5.** This compound was stopped in a trap cooled at −20°C. It was obtained in ~50%–55% yield. Spectral data obtained are: MS (Cl) [m/e (species) intensity]: 361 (M^+ + 1) 10.41, 341 (M^+ − F) 71.61, 325 (M^+ − Cl) 3.76, 275 (M^+ − CF_2Cl) 25.6, 180 ($C_3F_5ClN^+$) 13.46, 135 ($C_2F_4Cl^+$) 100, 85 (CF_2Cl^+) 51.4; IR (gas): 1744 s ($\nu_{C=N}$), 1277 w, 1220 vs, 1189 ms, 1121 s, 980 w, 964 ms, cm^{-1}; ^{19}F NMR: ϕ −22.24 (C, vbr t), −72.39 (A, dt), −94.69 (B, dt). J_{A-B} = 5.37 Hz, J_{A-C} = 4.03 Hz, J_{B-C} = 11.4 Hz.

Reaction of $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ with ClF to Form $CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl$ 6

Ten mmol of $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ and 65–70 mmol of ClF were condensed into a stainless steel vessel at −196°C. After being warmed to and remaining at 25°C for 10–12 h, the contents were separated via trap-to-trap. The addition product **6** was found in 60%–65% yield in a trap cooled at 0°C. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 261 (M^+ + 1 − 4 Cl) 7.48, 241 ($C_4F_5Cl_2N_2^+$) 47.1, 225 ($C_4F_6ClN_2^+$) 62.8, 130 ($C_2F_3ClN^+$) 69.3, 85 (CF_2Cl) 100; IR (liq): 1316 s, 1191 s, 1140 w, 1103 w, 1089 w, 1030 m, 1021 w, 1000 m, 962 ms, 917 m, 893 m, 874 m, 838 w, 799 ms, cm^{-1}; ^{19}F NMR: ϕ −29.6 to −35.3 (CF_2Cl, mult), −79.98 to −80.8, −94.3 to −95.2 (CFCl, mult) (four chiral centers).

Photolysis of 6 to Form $CF_2^AClN{=}CF^BCF{=}NCF_2Cl$ 7

Photolysis of five mmol of $CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl$ in a 1.8-L quartz vessel for 2 h formed **7**, which after trap-to-trap distillation, was isolated in a trap cooled at −40°C in 50%–55% yield. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 261 (M^+ + 1) 1.69, 241 (M^+ − F) 19.63, 225 (M^+ − Cl) 15.48, 190 (M^+ − 2Cl) 25.2, 171 ($C_4F_5N_2^+$) 11.80, 130 ($C_2F_3ClN^+$) 50.50, 85 (CF_2Cl^+) 100; IR (gas): 1734 vs ($\nu_{C=N}$), 1309 s, 1228 w, 1191 vs, 1153 w, 1113 s, 1047 s, 1008 vs, 552 m; ^{19}F NMR: ϕ −26.52 (B, t), −35.6 (A, d). J_{A-B} = 15.62 Hz. Anal. Calcd. for $C_4F_6Cl_2N_2$: C, 18.46, N, 10.77. Found: C, 18.56, N, 10.65.

Reaction of 4 and 5 with CsF to Form $CFCl_2CF_2\overline{NCF_2CF_2N{=}C}CFCl_2$ 8 and $CF_2ClCF_2\overline{NCF_2CF_2N{=}C}CF_2Cl$ 9

Five mmol of **4** or **5** was condensed over 8–10 mmol of CsF in a flask equipped with a Teflon stopcock and stirred for 8–10 h at 25°C. The resulting mixture of volatile materials was separated by trap-to-trap distillation.

Properties of $CF^ACl_2CF^B_2NCF^C_2CF^D_2N{=}CCF^ECl_2$ **8.** This compound was collected in ~75%–80% yield in a trap cooled at −10°C. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 393 ($M^+ + 1$) 22.89, 373 ($M^+ - F$) 26.65, 357 ($M^+ - Cl$) 33.84, 338 ($M^+ - ClF$) 8.32, 319 ($M^+ - ClF_2$) 6.16, 291 ($M^+ - CFCl_2$) 79.94, 241 ($M^+ - CF_2CFCl_2$) 8.85, 237 ($C_5F_6ClN_2^+$) 12.23, 151 ($C_2F_3Cl_2^+$) 70.71, 101 ($CFCl_2^+$) 100; IR (liq): 1636 s ($\nu_{C=N}$), 1368 s, 1331 s, 1256 vs, 1186 vs, 1143 s, 1007 ms, 927 s, 897 s, 858 s, 797 s, 687 s, cm^{-1}; ^{19}F NMR: ϕ −63.07, −63.48, −63.94, −64.34 (E, dt), −70.54 (A, dtt), −84.17 (B, dtd), −96.89 (C, dtt), −100.6 (D, s). J_{E-A} = 37.2 Hz, J_{E-B} = 37.0 Hz, J_{A-C} = 22.5 Hz, J_{A-B} = 7.1 Hz, J_{B-C} = 11.6 Hz, J_{C-D} = 1.32 Hz.

Properties of $CF^A_2ClCF^B_2NCF^C_2CF^D_2N{=}CCF^E_2Cl$ **9.** This compound was stopped in ~70%–75% yield in a trap cooled at −20°C. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 361 ($M^+ + 1$) 100, 341 ($M^+ - F$) 25.30, 325 ($M^+ - Cl$) 23.75, 275 ($M^+ - CF_2Cl$) 50.5, 230 ($C_4F_7ClN^+$) 38.38, 225 ($M^+ - C_2F_4Cl$) 43.98, 180 ($C_3F_5ClN^+$) 22.24, 164 ($C_3F_6N^+$) ($C_2F_4^+$) 38.44, 85 (CF_2Cl^+) 97.49; IR (gas): 1652 s ($\nu_{C=N}$), 1373 s, 1292 s, 1251 vs, 1206 vs. 1186 vs, 1139 ms, 1118 ms, 1003 ms, 967 ms, 846 s, 818 s, cm^{-1}; ^{19}F NMR: ϕ −58.15 (E, tt), −68.74, −68.92 (A, tt), −89.88 (B, tt), −97.88 (C, t), −100.4 (D, s). J_{E-B} = 19.53 Hz, J_{E-A} = 14.41 Hz, J_{B-C} = 10.0 Hz, J_{B-A} = ~0, J_{A-C} = 14.41 Hz.

Reaction of **7** *with CsF to Form $CF_2CF_2N(CF_3)CF_2N{-}C{=}NCF_2N(CF_3)CF_2$* **1**

Five mmol of $CF_2ClN{=}CFCF{=}NCF_2Cl$ was condensed into a flask that contained excess anhydrous CsF and the mixture was stirred at 100°C for 6–8 h. The volatile products were separated by trap-to-trap distillation. Compound **1** was collected in the trap cooled at −30°C and was confirmed by comparison with literature data [8].

Reaction of $Cl_2CFCF_2NCF_2CF_2N{=}CCFCl_2$ **8** *with ClF to form $Cl_2CFCF_2NCF_2CF_2N(Cl)CFCFCl_2$* **10**

Five mmol of **8** and 7–8 mmol of ClF were condensed into a stainless steel vessel at −196°C. The contents were allowed to warm to 25°C and remain for 10–12 h, and were separated by trap-to-trap distillation. Compound **10** remained as an involatile liquid in 80%–85% yield in the reaction vessel. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 427 ($M^+ - F$) 0.32, 411 ($M^+ - Cl$) 0.22, 373 ($M^+ - ClF_2$) 19.72, 357 ($C_6F_8Cl_3N_2^+$) 21.65, 291 ($C_5F_7Cl_2N_2^+$) 76.54, 151 ($CF_2CFCl_2^+$) 94.85, 101 ($CFCl_2^+$) 100; IR (liq): 1381 vs, 1300 s, 1274 s, 1246 s, 1152 s, 1100 s, 987 s, 904 vs, 853 s, 812 s, 778 s, 737 s, 709 s, cm^{-1}; ^{19}F NMR: very complex series of multiplets ranging from ϕ −62.26 to −107.7.

Photolysis of **10** *to form $F^EC{=}NCF^D_2CF^C_2NCF^B_2CCl_2F^A$* **11**

Five mmol of 10 was condensed into a quartz vessel and photolyzed at 3000 Å for 2–3 h. After trap-to-trap separation of the products, **11** was obtained in ~70%–75% yield in a trap cooled at −35°C. The other major product is $CFCl_3$ identified by its ^{19}F NMR resonance at ϕ 0. Spectral data obtained for **11** are: MS (CI) [m/e (species) intensity]: 311 ($M^+ + 1$) 76.22, 291 ($M^+ - F$) 68.01, 275 ($M^+ - Cl$) 35.93, 209 ($M^+ - CFCl_2$) 79.09, 159 ($M^+ - CF_2CFCl_2$) 100, 151 ($CF_2CFCl_2^+$) 36.96, 101 ($CFCl_2^+$) 18.61; IR (gas): 1723, 1719 d, vs ($\nu_{C=N}$), 1423 vs, 1364 ms, 1279 s, 1260 s, 1198 s, 1162 w, 1111 ms, 931 w, 911 w, 792 ms, cm^{-1}; ^{19}F NMR: ϕ −66.77, −66.95, −67.12 (E, ddt), −73.96, −74.36 (A, mult), −92.37 (B, dt), −95.71, −96.11 (C, D, d, t). $J_{A=B}$ = 35.8 Hz, J_{B-C} = 19.2 Hz, J_{D-A} = J_{C-A} = 34.6 Hz. Anal. Calcd. for $C_5F_8Cl_2N_2$: C, 19.35, N, 9.03. Found: C, 19.31, N, 9.01.

Reaction of **11** *with ClF to form $CF^A_2N(Cl)CF^B_2CF^C_2NCF^D_2CCl_2F^E$* **12**

Five mmol of $Cl_2CFCF_2NCF_2CF_2N{=}CF$ **11** was condensed with 6–7 mmol of ClF into a stainless steel vessel at −196°C. After the vessel was held at 25°C for 6–8 h and contents were separated, **12** was isolated in ~80% yield in a trap cooled at −10°C. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 345 ($M^+ - F$) 1.36, 329 ($M^+ - Cl$) 0.72, 291 ($C_5F_7Cl_2N_2^+$) 51.38, 275 ($C_5F_8ClN_2^+$) 38.54, 209 ($C_4F_7N_2^+$) 100, 159 ($C_3F_5N_2^+$) 38.92; IR (liq): 1382 s, 1327 s, 1284 s, 1158 s, 1099 s, 1009 s, 929 s, 904 s, 862 s, 741 s, 696 ms, 654 s, 608 s, 464 s, cm^{-1}; ^{19}F NMR: ϕ −67.93 (E, mult), −75.17 (A, mult), −89.88 (B, mult), −101.53 (C, D, mult). Anal. Calcd. for $C_5F_9Cl_3N_2$: C, 16.48, N, 7.69. Found: 16.45, N, 7.62.

Photolysis of **12** to form $CF^A_2CF^B_2N(CF^C_2CCl_2F^D)CF^E_2N{-}NCF_2N(CF_2CCl_2F)CF_2CF_2$ **13**

Five mmol of $Cl_2CFCF_2NCF_2CF_2N(Cl)CF_2$ **12** was condensed into a 200-mL quartz flask and was irradiated at at 3000 Å for 2–3 h. Chlorine was the major volatile compound and **13** remained in the flask as an involatile liquid. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 639 ($M^+ - F$) 22.66, 623 ($M^+ - Cl$) 16.81, 557 ($M^+ - CFCl_2$) 50.25, 424 ($C_7F_{12}Cl_2N_3^+$) 20.54, 362 ($C_8F_{11}N_4^+ + 1$) 100, 151 ($CF_2CFCl_2^+$) 77.73, 101 ($CFCl_2^+$) 17.24; IR (liq): 1376 ms, 1328 s, 1299 s, 1212 s, 1155 s, 1099 s, 1007 s, 966 vs, 927 s, 903 s, 784 s, 751 s, 703 s, 542 s, cm^{-1}; ^{19}F NMR: ϕ −61.50, −63.01, −65.44, −66.77, (E, mult), −75.06 (D, mult), −86.99, −87.97, −89.77, −90.81, −92.26, −93.07, −94.11, −94.98 (A, B, mult), −98.17, −98.4, −99.96 (C, mult), Anal. Calcd. for $C_{10}F_{18}Cl_4N_4$: C, 18.24, N, 8.51. Found: C, 18.21, N, 8.50.

Reaction of **1** *with ClF to form* $CF_2CF_2(CF_3)NCF_2N{-}CFCF_2N(CF_3)CF_2N(Cl)$ **14**

Five mmol of 1 and 6 mmol of ClF were condensed into a stainless steel vessel at −196°C, warmed to and held at 25°C for 6–8 h. After trap-to-trap distillation, **14** was collected in a trap cooled at −10°C (~80% yield). Spectral data obtained are: MS (CI) [m/e (species) intensity]: 437 ($M^+ - ClF_2$) 1.35, 342 ($C_6F_{12}N_3^+$) 0.38, 323 ($C_6F_{11}N_3^+$) 1.46, 304 ($C_6F_{10}N_3^+$) 0.52, 254 ($C_5F_8N_3^+$) 0.93, 228 ($C_4F_8N_2^+$) 2.40, 209 ($C_4F_7N_2^+$) 22.12, 159 ($C_3F_5N_2^+$) 20.05, 114 ($C_2F_4N^+$) 25.64, 95 ($C_2F_3N^+$) 73.83, 69 (CF_3^+) 100; IR (liq): 1414 sh, 1337 br, 1297 sh, 1257 sh, 1197 br, 1085 m, 994 ms, 928 s, 898 ms, 694 ms, cm^{-1}; ^{19}F NMR: ϕ −55.89 (CF_3, mult) −60.23, −61.16, −62.55, −73.26, −74.65, −82.0, −87.04, −89.01, −91.85, −110.85 (mult).

Photolysis of **14** *to form*

$$\begin{array}{ccc} CF_2N(CF_3)CF_2CFN{-}NCFCF_2N(CF_3)CF_2 \\ CF_2CF_2N(CF_3)CF_2N \qquad NCF_2N(CF_3)CF_2CF_2 \end{array}$$

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Five mmol of **14** in a quartz vessel was photolyzed at 3000 Å for 4–5 h to break the N—Cl bond producing Cl_2 and **15** (~20%–25% yield) was found as an involatile liquid in the reaction flask. Spectral data obtained are: MS (CI) [m/e (species) intensity]: 748 ($C_{13}F_{26}N_7^+$) 0.18, 703 ($C_{12}F_{25}N_6^+$) 2.5, 653 ($C_{11}F_{23}N_6^+$) 1.29, 570 ($C_{10}F_{20}N_5^+$) 50.15, 475 ($C_8F_{17}N_4^+$) 94.91, 392 ($C_7F_{14}N_3^+$) 47.7, 342 ($C_6F_{12}N_3^+$) 57.31, 209 ($C_4F_7N_2^+$) 79.3, 159 ($C_3F_5N_2^+$) 31.56, 114 ($C_2F_4N^+$) 81.82, 69 (CF_3^+) 100; IR (liq): 1408 sh w, 1348 br, 1256 w, 1201 br, 1155 sh, 1087 m, 1018 ms, 926 s, 895 ms, 778 ms, 699 s, cm^{-1}; ^{19}F NMR: A series of broad multiplets from −58.2 to −93.8. Anal. Calcd. for $C_{16}F_{34}N_8$: C, 20.21, N, 11.79. Found: C, 20.20, N, 11.68.

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