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Syntheses of (Difluoroamino)difluoroacetonitrile, *syn*-Fluoro(fluoroimino)acetonitrile, and *syn*-3,3,3-Trifluoro-2-(fluoroimino)propanenitrile and Their Reactions with Chlorine Fluoride. Syntheses of New Perfluorinated Diazines

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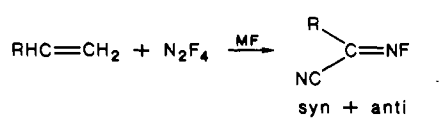
Tetrafluorohydrazine, when added to the olefins $CF_2{=}CH_2$, $CFH{=}CH_2$, and $CF_3CH{=}CH_2$ in the presence of KF, gave (difluoroamino)difluoroacetonitrile, F_2NCF_2CN, *syn*-fluoro(fluoroimino)acetonitrile, $FC({=}NF)CN$, and *syn*-3,3,3-trifluoro-2-(fluoroimino)propanenitrile, $CF_3C({=}NF)CN$, respectively. Reaction of chlorine fluoride with these compounds led to *N,N*-dichloro-*N'*,*N'*,1,1,2,2-hexafluoro-1,2-ethanediamine, $F_2NCF_2CF_2NCl_2$, *N,N,N'*-trichloro-*N'*,1,1,2,2-pentafluoro-1,2-ethanediamine, $ClFNCF_2CF_2NCl_2$, *N,N*-dichloro-1,1,3,3,3-pentafluoro-2-(fluoroimino)propanamine, $CF_3C({=}NF)CF_2NCl_2$, and *N,N,N'*-trichloro-*N'*,1,1,2,3,3,3-heptafluoro-1,2-propanediamine, $CF_3CF(NClF)CF_2NCl_2$, respectively. Photolysis of the chloroamine compounds $F_2NCF_2CF_2NCl_2$, $CF_3({=}NF)CF_2NCl_2$, $ClFNCF_2CF_2NCl_2$, and $CF_3CF(NClF)CF_2NCl_2$ gave the azo derivatives 1,1'-azobis(*N,N*,1,1,2,2-hexafluoro-2-ethanamine), $F_2NCF_2CF_2N{=}NCF_2CF_2NF_2$, 1,1'-azobis(*N*,1,1,3,3,3-hexafluoro-2-propanimine), $CF_3C({=}NF)CF_2N{=}NCF_2C({=}NF)CF_3$, 2,2'-azobis(*N*-chloro-*N*,1,1,2,2-pentafluoroethanamine), $ClFNCF_2CF_2N{=}NCF_2CF_2NClF$, and 1,1'-azobis(*N*-chloro-*N*,1,1,2,3,3,3-heptafluoro-2-propanamine), $CF_3CF(NClF)CF_2N{=}NCF_2(NClF)CFCF_3$, respectively.

Introduction

Highly fluorinated nitrogen compounds that contain the $-NF_2$, $-NCl_2$, $-NFCl$, and/or $-N{=}N-$ functionalities are very reactive synthetic reagents and are potentially explosive materials.[1] Tetrafluorohydrazine, N_2F_4, has had a major impact on the development of the fluoronitrogen field.[2]

Of particular interest are the reactions of N_2F_4 with certain olefins that when carried out in the presence of an alkali-metal fluoride gave (fluoroimino)acetonitriles:[3-6]



R = CN, F, CF_3, C_6H_5, CH_3, $COOCH_3$, SF_5, $CH_2OC(O)CH_3$
M = Na, K, Cs

The reactions of these fluoroimino nitriles and related compounds with nucleophiles have been studied in detail, with use of such species as NH_3, HN_3, RONa,[3] $C_2H_5NH_2$, $(C_2H_5)_2NH$, and C_2H_5OH.[5] However, addition reactions to both the $-C{\equiv}N$ and the $>C{=}NF$ bonds in these compounds have not been studied.

Chlorine fluoride added readily across carbon-nitrogen multiple bonds; e.g., when it was added to trifluoroacetonitrile, dichloro(pentafluoroethyl)amine resulted:[7]

$$CF_3CN + 2ClF \rightarrow CF_3CF_2NCl_2$$

Such dichloro(perhaloalkyl)amines are useful synthetic reagents, and many compounds of the type R_fNCl_2[8] and R_fNF_2[1c,d] have been prepared. Mixed chlorofluoro(fluoroalkyl)amines, R_fNClF, are another potentially useful class of reagents. Chlorine fluoride added readily to $R_fR_f'C{=}NF$ when $R_f = R_f' = Cl$ and/or F.[9] However, when $R_f = R_f' = CF_3$, CsF was required to catalyze the reaction.

$$R_fR_f'C{=}NF + ClF \rightarrow R_fR_f'FCNClF$$

$$R_f = R_f' = CF_3, Cl, F$$

$$R_f = Cl;\ R_f' = F$$

CH_3CF_2NClF was obtained from CH_3CN and ClF_5:[10]

$$CH_3CN + ClF_5 \rightarrow CH_3CF_2NClF$$

Recently there has been renewed interest in these types of compounds due to a report of a new high-yield synthesis from the reaction of nitriles with a mixture of ClF and F_2:[11]

$$RCN + ClF + F_2 \rightarrow RCF_2NClF$$

$$R = Cl, CF_3, CF_3CF_2, CCl_3, CH_3$$

This method involves either the addition of fluorine to $RCF{=}NCl$ or the fluorination of $RNCl_2$ to RNClF.

These chlorofluoro(perhaloalkyl)amines have been used as precursors to fluoroimines and fluoroamines[12] via a dehalogenation reaction with mercury:

$$RCF_2NClF \xrightarrow{Hg} RCF{=}NF$$

$$R = Cl, CF_3, CF_3CF_2$$

$$RCF_2NClF \xrightarrow[Hg]{TFA} RCF_2NHF$$

$$R = Cl, F, CF_3, CF_3CF_2$$

$$NF_2CFCl_2 + Hg \xrightarrow{100\ ^\circ C} syn\text{- and } anti\text{-}FN{=}CFCl^{13}$$

In this paper are described one-pot, high-yield syntheses of (difluoroamino)difluoroacetonitrile, *syn*-fluoro(fluoroimino)acetonitrile, and *syn*-3,3,3-trifluoro-2-(fluoroimino)propanenitrile and their reactions with chlorine fluoride to give *N,N*-dichloro-*N,N'*,1,1,2,2-hexafluoro-1,2-ethanediamine, *N,N,N'*-trichloro-

(1) For reviews on fluorinated nitrogen compounds see: (a) Banks, R. E.; Barlow, M. G. *Fluorocarbon Relat. Chem.* **1971**, *1*, 98. *Ibid.* **1974**, *2*, 204. **1976**, *3*, 207. (b) Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; MacDonald: London, 1970. (c) Freeman, J. P. *Adv. Fluorine Chem.* **1970**, *6*, 287. (d) Ruff, J. K. *Chem. Rev.* **1967**, *67*, 665.
(2) Colburn, C. B.; Kennedy, A. *J. Am. Chem. Soc.* **1958**, *80*, 5004.
(3) Logothetis, A. L.; Sausen, G. N. *J. Org. Chem.* **1966**, *31*, 3689.
(4) Dyatkin, B. L.; Makarov, K. N.; Knunyants, I. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1968**, *635*, 1081.
(5) Dyatkin, B. L.; Makarov, K. N.; Knunyants, I. L. *Tetrahedron* **1971**, *27*, 51.
(6) Ross, D. L.; Coon, C. L.; Hill, M. E.; *J. Org. Chem.* **1970**, *35*, 3093.
(7) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.
(8) Schack, C. J.; Christe, K. O. *Isr. J. Chem.* **1978**, *17*, 20 and references therein.
(9) Swindell, R. F.; Zaborowski, L. M.; Shreeve, J. M. *Inorg. Chem.* **1971**, *10*, 1635.
(10) Lustig, M. *Inorg. Chem.* **1967**, *6*, 1064.
(11) Sekiya, A.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1979**, *101*, 7640. Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1981**, *20*, 1.
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N',1,1,2,2-pentafluoro-1,2-ethanediamine, *N,N*-dichloro-1,1,3,3,3-pentafluoro-2-(fluoroimino)propanamine, and *N,N,-N'*-trichloro-*N'*,1,1,2,3,3,3-heptafluoro-1,2-propanediamine, respectively. Photolysis of these compounds gave the respective diazines.

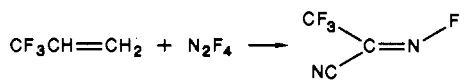
Results and Discussion

(Difluoroamino)difluoroacetonitrile (I) has been prepared by the photolysis of cyanogen with N_2F_4[14] or by the reaction of trifluoroethylene and N_2F_4 in the presence of acetonitrile and potassium fluoride.[4] This method has been used in the synthesis

$$N{\equiv}C{-}C{\equiv}N + N_2F_4 \xrightarrow{UV} F_2NCF_2CF_2NF_2 + F_2NC_2F_5 + CF_4 + NF_3 + N_2F_2 + \underset{\text{I (26\%)}}{F_2NCF_2CN}$$

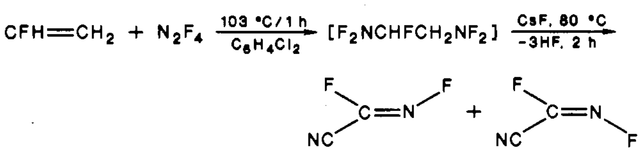
$$CF_2{=}CH_2 + N_2F_4 \xrightarrow[\text{CH}_3\text{CN, 160 °C/20 h}]{\text{KF/}-2\text{HF}} \text{I (69\%)}$$

of *syn*-3,3,3-trifluoro-2-(fluoroimino)propanenitrile (II).[5] With



II (71%)

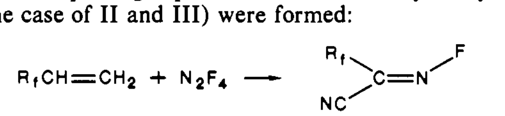
use of the same route, i.e., addition of $\cdot NF_2$ radicals across the double bond followed by the elimination of HF in the presence of a base, both the syn and anti isomers of fluoro(fluoroimino)-acetonitrile (III) were prepared in rather low yield (35%) and by



syn 3 : anti 1

III

a rather hazardous procedure.[3] Thus, in order to study the reactions of these N_2F_4 derivatives (I–III), we were prompted to synthesize them in one-pot reactions carried out at high temperature for prolonged periods in order that only the syn isomers (in the case of II and III) were formed:



syn only

II: $R_f = CF_3$ (~70%)
III: $R_f = F$ (~80%)

$$CF_2{=}CH_2 + N_2F_4 \xrightarrow[160\ °C/\sim 40\ h]{KF} \underset{\text{I (}\sim\text{80\%)}}{F_2NCF_2CN}$$

We found that a solvent was not necessary. Presumably only the syn isomers of II and III are obtained because they are more stable thermally than the anti isomer. The ^{19}F NMR spectrum confirms the syn isomer assignment by the small coupling constant value for J_{NF-R_f} (J_{NF-CF_3} = 9.96 Hz in II and J_{NF-CF} = 53.8 Hz in III). The J_{NF-R_f} value for the anti isomer would be expected to be >200 Hz. Examples of these J values are in the literature.[3,12,15,16] The NF and NF_2 resonance bands are broad singlets due to the nuclear quadrupole broadening effect of the nitrogen. The infrared spectra of I–III have strong absorption bands around 2300 cm^{-1}, which are assigned to $\nu_{C\equiv N}$. II and III have $\nu_{C=N}$ bands in the 1650-cm^{-1} region. Compounds I–III are highly volatile, colorless liquids.

The reaction of I with chlorine fluoride proceeded easily to give *N,N*-dichloro-*N',N'*,1,1,2,2-hexafluoro-1,2-ethanediamine (IV).

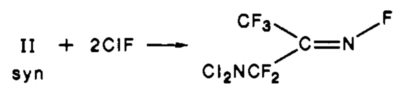
$$F_2NCF_2CN + 2ClF \rightarrow \underset{\text{IV (80\%)}}{F_2NCF_2CF_2NCl_2}$$

Dimerization of IV, by ultraviolet photolysis through quartz, gave the diazine V as a yellow liquid that we believe to be one of the

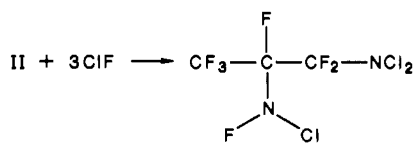
$$2F_2NCF_2CF_2NCl_2 \xrightarrow[-2Cl_2]{UV/2.5\ h} \underset{\text{V (96\%)}}{F_2NCF_2CF_2N{=}NCF_2CF_2NF_2}$$

first examples of an azobis(perfluoroalkanamine) compound. The ^{19}F NMR spectrum of IV showed coupling between both the chemically nonequivalent CF_2 groups as well as with the NF_2 group. Upon dimerization to V, the $J_{CF_2-CF_2}$ coupling disappeared. This was also observed for $CF_3CF_2NCl_2$ and its dimer $CF_3CF_2N{=}NCF_2CF_3$.

The reaction of II with chlorine fluoride proceeded in a stepwise manner, which indicates that selective addition occurs. Addition of 2 equiv of chlorine fluoride resulted in attack at the carbon–nitrogen triple bond only to leave the carbon–nitrogen double bond intact. The addition of 3 equiv of chlorine fluoride led to complete saturation of both multiple bonds.

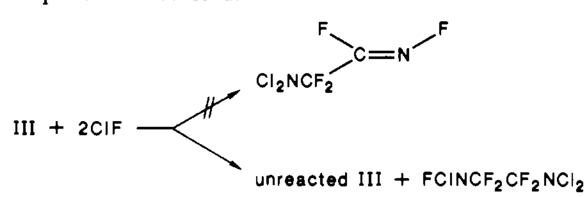


VI, syn



VII

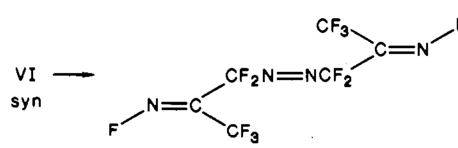
However, in the case of III, addition of ClF is not selective; i.e., regardless of the stoichiometry used, saturation of both multiple bonds occurred.



VIII

$$\text{III} + 3ClF \longrightarrow \text{VIII}$$

The difference in the behavior of II and III with ClF must arise from the difference in polarity of the >C=N– and N≡C– bonds. In III, there is presumably little difference between the polarity of the two bonds so that the attack by ClF occurred at both bonds simultaneously. In II the presence of the CF_3 group decreases the polarity of the >C=NF bond relative to that of the –C≡N bond, and therefore, addition occurred initially at the latter bond. When this was essentially complete, saturation of the other bond occurred. The UV photolysis of VI led to the dimer IX (syn isomer



IX, syn

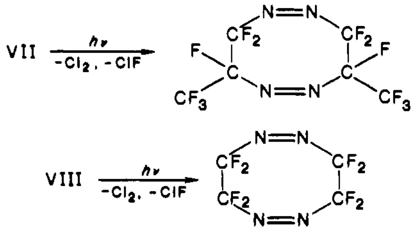
only). The chemical shifts in the ^{19}F NMR spectra of the azo compounds V and IX change little from those of their parent *N,N*-dichloro compounds. All of the azo compounds are yellow and are of low volatility.

The photolysis of the trichloroperfluoroalkanediamines VII and VIII could lead to some interesting possibilities since CF_3NClF dimerizes with the loss of ClF upon photolysis:[17]

$$CF_3NClF \xrightarrow{h\nu} CF_3N{=}NCF_3 + 2ClF$$

(14) Dresdner, R. D.; Merritt, J.; Royal, R. P. *Inorg. Chem.* **1965**, *4*, 1228.
(15) Dybvig, D. H. *Inorg. Chem.* **1966**, *5*, 1795.
(16) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon: Oxford, England, 1977.
(17) Hynes, J. B.; Bishop, B. C.; Bigelow, L. A. *Inorg. Chem.* **1967**, *6*, 417.

Therefore, in VII and VIII dimerization and ring closure are possible. While this may have happened, we were unable to confirm the existence of these cyclic bis(diazines).



The photolysis of VII and VIII led to yellow liquids of low volatility. Upon trap-to-trap distillation, chlorine and a number of unidentified volatile products were found in the trap at −196 °C. Gas chromatography showed that in each case the yellow liquids consisted of at least seven components. By spectroscopic means, 1,1′-azobis(*N*-chloro-*N*,1,1,2,3,3,3-heptafluoro-2-propanamine) (X) and 2,2′-azobis(*N*-chloro-*N*,1,1,2,2-pentafluoroethanamine) (XI) were identified from the mixture, but it was not possible to

$$\mathrm{VII} \xrightarrow{h\nu} \underset{\textbf{X}}{CF_3CF(NClF)CF_2N{=}NCF_2CF(NClF)CF_3}$$

$$\mathrm{VIII} \xrightarrow{h\nu} \underset{\textbf{XI}}{FClNCF_2CF_2N{=}NCF_2CF_2NClF}$$

purify them sufficiently to obtain elemental analysis data. The reactions of VII and VIII with mercury were studied. The only reaction appeared to be chemisorption to form some unknown mercury derivative. Similar reactions have been observed with mercury and other chlorofluoroalkylamines.[12]

Experimental Section

Materials. The partially fluorinated olefins were used as received from commercial suppliers without further purification. Sources were as follows: 1,1-difluoroethylene, 3,3,3-trifluoropropene, and trifluoroethylene, PCR; tetrafluorohydrazine, Air Products; chlorine fluoride, Ozark-Mahoning. Potassium fluoride (Aldrich) was dried at 160 °C for 2 days prior to use.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum system equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively by using PVT techniques. Products were separated by fractional condensation (trap-to-trap distillation). Final purification of the compounds was achieved on a Hewlett-Packard 5710A gas chromatograph. Various liquid phases were used on either Chromosorb P or W. All columns were constructed from $^1/_4$ in. o.d. copper tubing. Photolysis reactions were accomplished by using a Hanovia utility ultraviolet quartz lamp. Infrared spectra were recorded with a Perkin-Elmer 599B or a 1710 infrared Fourier transform spectrometer by using a 10-cm cell equipped with KBr windows or a KBr liquid film cell. ^{19}F NMR spectra were obtained on either a JEOL FX-90Q Fourier transform NMR spectrometer operating at 84.26 MHz or a Varian EM-360L NMR spectrometer operating at 54.6 MHz by using $CDCl_3$ as a solvent and $CFCl_3$ as an internal or external reference. The ^{19}F NMR spectral data for VII and VIII were obtained at 338.7 MHz on a Nicolet NT-360 NMR spectrometer. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with a VG 7070 HS mass spectrometer. Methane was the ionizing gas used for chemical ionization mass spectra. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany. Slush baths were made as follows: −137 °C, 35:60 petroleum ether–liquid N_2; −98 °C, methanol–liquid N_2; −78 °C, ethanol–dry ice; −40 °C, 4:3 ethanol–water (by volume) with liquid N_2. *Caution! Care is essential when handling N_2F_4 and its derivatives. Reactions should be carried out on a small scale, and adequate shielding is essential during all stages of the procedures. Any apparatus used should be free of organic materials. Nitrogen–halogen compounds are known to exhibit explosive properties, and indeed a number of explosions have occurred when handling some of the compounds described below.*

Reaction of Olefins with N_2F_4. To a hot, dry, 75-mL stainless steel Hoke cylinder was added ∼4 g of dried KF and three small-diameter steel balls. The cylinder was fitted with a stainless steel Hoke valve and evacuated as it cooled. Into the cylinder, cooled to −196 °C, was condensed 6 mmol of olefin followed by 7 mmol of N_2F_4. The cylinder was allowed to warm to room temperature and then heated at 160 °C for ∼40 h. The cylinder was shaken occasionally. The products were separated by trap-to-trap distillation.

Properties of F_2NCF_2CN (I). The compound was found in the trap at −137 °C, having passed through a trap at −98 °C. It was obtained in ∼80% yield as a colorless gas. The gas-phase infrared spectrum had bands at 2280 (m) ($\nu_{C≡N}$), 1230 (br, vs), 1155 (m), 1000 (ms), and 950 (s) cm^{-1} (ν_{N-F}). The ^{19}F NMR spectrum had a broad singlet at ϕ 29.7 (NF_2) and a singlet at ϕ −89.7 (CF_2).

Properties of *syn*-$CF_3C(=NF)CN$ (II). The compound was found in the trap at −98 °C, having passed through a trap at −60 °C. It was obtained in ∼70% yield as a colorless volatile liquid. Further purification was achieved on a 23-ft Kel-F #3 on Chromosorb P gas chromatographic column, but this was not necessary in order to study the reactions of this compound. The gas-phase infrared spectrum showed bands at 2251 (m) ($\nu_{C≡N}$), 1610 (m) ($\nu_{C=N}$), 1347 (vs), 1235 (vs), 1197 (vs), 1105 (vs), and 956 (vs) cm^{-1}. The ^{19}F NMR spectrum consisted of a broad singlet at ϕ 74.5 (NF) and a doublet centered at ϕ −65.95 (CF_3), with J_{CF_3-NF} = 9.96 Hz and some additional unexplained fine structure. The CI^+ mass spectrum showed an M + 1 peak at *m/e* 141 (27.4%). Other fragments were *m/e* 121 (M^+ − F, 10.9%), 107 ($CF_3C_2N^+$, 0.4%), 71 ($M^+ - CF_3$, 1.3%), and 69 (CF_3^+, 100%).

Properties of *syn*-$FC(=NF)CN$ (III). The compound was found in the trap at −98 °C, having passed through a trap at −78 °C. It was obtained in ∼80% yield as a colorless volatile liquid. Further purification was achieved on a 23-ft Kel-F #3 on Chromosorb P gas chromatographic column, but this was not necessary in order to study the reactions of this compound. The gas-phase infrared spectrum showed bands at 2282 (m) ($\nu_{C≡N}$), 1650 (d, m) ($\nu_{C=N}$), 1314 (s), 1300 (s), 1190 (w), 1080 (w), and 990 (w) cm^{-1} (ν_{N-F}). The ^{19}F NMR spectrum showed a singlet at ϕ 6.5 (NF) and a doublet at ϕ −60.9 (CF), with J_{NF-CF} = 53.8 Hz. The CI^+ mass spectrum had the base peak as the molecular ion: *m/e* 91 (M^+ + 1, 100%). Other fragments were *m/e* 90 (M^+, 40.2%), 71 (M^+ − F, 36.7%), and 69 (CF_3^+, 11.2%).

Preparation of $F_2NCF^b{}_2CF^a{}_2NCl_2$ (IV). Into an evacuated 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve were condensed 7.5 mmol of F_2NCF_2CN and 17 mmol of ClF at −196 °C. The cylinder was placed in a slush bath at −78 °C and allowed to warm slowly to ∼−10 °C over 12 h. Trap-to-trap distillation gave IV in the trap at −78 °C as a pale yellow liquid (vp ≈ 40 torr at 25 °C) in ∼60% yield. Final purification was by gas chromatography on a 12 ft QF-1 Chromosorb P column at 70 °C. The gas-phase infrared spectrum had bands at 1328 (ms), 1265 (vs), 1223 (vs), 1155 (vs), 1085 (s), 1048 (ms), 990 (s), 950 (vs), 855 (m), 755 (m), and 655 (w) cm^{-1}. The ^{19}F NMR spectrum showed a broad peak at ϕ 19.2 (NF_2), a triplet at ϕ −95 ($CF^b{}_2$), and a broad singlet at ϕ 109 ($CF^a{}_2$), with $J_{NF_2-CF^b{}_2}$ = 8.5 Hz and $J_{CF_2-CF_2}$ = 1.5 Hz. The EI^+ mass spectrum showed a molecular ion and an appropriate fragmentation pattern (ratios are given for the ^{35}Cl- and ^{37}Cl-containing ions): *m/e* 238/236 (M^+, 1.3/2.2%), 136/134 ($CF_2NCl_2^+$, 6.1/9.5%), 132/130 ($C_2F_3NCl^+$, 19.8/61.7%), 114 ($F_2NC_2F_2^+$, 3.5%), 102 ($F_2NCF_2^+$, 1.5%), 101/99 (CF_2NCl^+, 1.7/5.9%), 100 ($C_2F_4^+$, 7.4%), 82/80 ($CFNCl^+$, 13.7/43.9%), 81 ($C_2F_3^+$, 1.8%), 69 (CF_3^+, 100%), 50 (CF_2^+, 26.9%), 37/35 (Cl^+, 1.3/5.3%), 31 (CF^+, 19.4%), and 28 (N_2^+, 97.4%). Anal. Calcd for $C_2F_6N_2Cl_2$: C, 10.14; F, 48.1; Cl, 29.90. Found: C, 9.51; F, 49.8; Cl, 29.03.

Preparation of $F_2NCF^b{}_2CF^a{}_2N{=}CF^a{}_2CF^b{}_2NF_2$ (V). A 300-mL quartz vessel equipped with a Kontes Teflon stopcock was evacuated, and 2.9 mmol of $F_2NCF_2CF_2NCl_2$ was condensed into it at −196 °C. After the flask was warmed to 25 °C, it was placed about 60 cm from a Hanovia Utility UV lamp. After photolysis for 2.5 h and trap-to-trap distillation, a yellow liquid was found in the trap at −78 °C. The material, $F_2NCF_2CF_2N{=}NCF_2CF_2NF_2$, was obtained in ∼93% yield and had a vapor pressure of ∼40 torr at 25 °C. Final purification could be achieved by gas chromatography on a 23-ft Kel-F #3 on Chromosorb P column at 25 °C. The gas-phase infrared spectrum had bands at 1315 (m), 1253 (vs), 1209 (s), 1178 (s), 1148 (s), 1072 (m), 979 (m), 944 (s), and 742 (mw) cm^{-1}. The ^{19}F NMR spectrum showed a broad singlet at ϕ 17.7 (NF_2), a triplet at ϕ −107.5 ($CF^b{}_2$), and a singlet at ϕ −116.3 ($CF^a{}_2$), with $J_{CF^b{}_2-NF_2}$ = 9 Hz. The CI^+ mass spectrum showed a molecular ion of low intensity at *m/e* 333 (M^+ + 1, 0.2%). Other fragments were *m/e* 313 (M^+ − F, 1.3%), 280 ($M^+ - NF_2$, 0.8%), 166 ($F_2NCF_2CF_2N^+$, 2.1%), 128 ($CF_2NNCF_2^+$, 0.3%), 119 ($C_2F_5^+$, 8.1%), 114 ($C_2F_4N^+$, 7.3%), 102 (CF_3NF^+, 0.7%), 100 ($C_2F_4^+$, 19.7%), and 81 ($C_2F_3^+$, 2.7%). The EI^+ mass spectrum did not show a molecular ion, but the following fragments were observed: *m/e* 119 ($C_2F_5^+$, 7.9%), 114 ($C_2F_4N^+$, 4.6%), 100 ($C_2F_4^+$, 27.4%), 81 ($C_2F_3^+$, 2.6%), 69 (CF_3^+, 100%), 52 (NF_2^+, 0.2%), 50 (CF_2^+, 10.5%), 31 (CF^+, 9.9%), and 28 (N_2^+, 41.2%).

Preparation of *syn*-$CF_3C(=NF)CF_2NCl_2$ (VI). Into an evacuated 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve were condensed 15 mmol of $CF_3C(=NF)CN$ and 30 mmol of ClF at −196 °C. The cylinder was placed in a slush bath at −78 °C and held at that temperature for ~5 h. It was then allowed to warm slowly to ~−10 °C over 12 h. Trap-to-trap distillation gave $CF_3C(=NF)CF_2NCl_2$ in the trap at −40 °C. The colder trap contained a small amount of $CF_3C(=NF)CF_2NCl_2$, some unreacted $CF_3C(=NF)CN$, Cl_2, SiF_4, and some unidentified products. On the basis of the amount of $CF_3C(=NF)CN$ consumed, VI was obtained as a colorless liquid, having a vapor pressure of ~30 torr at 25 °C in a yield of ~46%. Final purification was accomplished by gas chromatography on a 12-ft silicone SE-52 on Chromosorb W column. The liquid-phase infrared spectrum showed bands at 1635 (m), 1335 (vs), 1250 (vs), 1205 (vs), 1163 (s), 1135 (s), 1040 (m), 1018 (vs), 960 (vs), 850 (w), 750 (s), and 645 (m) cm^{-1}. The ^{19}F NMR spectrum consisted of a broad singlet at ϕ 56.4 (NF), a four-line pattern (due to two overlapping triplets) at ϕ −63.1 (CF_3), and at ϕ −82.7 (CF_2) a six-line pattern (due to overlapping quartets), with $J_{CF_3-NF} \simeq J_{CF_3-CF_2} \simeq 9$ Hz. The EI^+ mass spectrum showed a molecular ion and an appropriate fragmentation pattern (ratios are given for the ^{35}Cl- and ^{37}Cl-containing ions): *m/e* 252/250/248 (M^+, 0.1/1.6/2.6%), 196/194 ($M^+ - ClF$, 8.8/25.8%), 114 (CF_3CNF^+, 4.2%), 101/99 (CF_2NCl^+, 4.5/13.7%), 82/80 ($CFNCl^+$, 7.3/23/2%), 69 (CF_3^+, 100%), and 50 (CF_2^+, 6.2%). Anal. Calcd for $C_3F_6N_2Cl_2$: C, 14.47; F, 45.8; Cl, 28.48. Found: C, 14.58; F, 45.1; Cl, 28.18.

Preparation of $CF_3CF(NClF)CF_2NCl_2$ (VII). This was accomplished by using the same method as for VI except that the amount of $CF_3C(=NF)CN$ and ClF used were 10 and 35 mmol, respectively. Trap-to-trap distillation gave $CF_3CF(NClF)CF_2NCl_2$ as a nearly colorless liquid of very low volatility in ~92% yield in the trap at −40 °C. Final purification was achieved by gas chromatography on a 5-ft OV-1 on Chromosorb P column at 25 °C. The liquid-phase infrared spectrum had bands at 1282 (br, vs), 1233 (br, vs), 1181 (vs), 1147 (vs), 1110 (vs), 1065 (vs), 984 (vs), 964 (vs), 911 (s), 878 (vs), 828 (s), 746 (vs), 713 (vs), 635 (m), 582 (w), 551 (w), and 507 (w) cm^{-1}. The ^{19}F NMR spectrum for $CF_3C^*F(N^*ClF)CF_AF_BNCl_2$ (mixture of diastereoisomers) was analyzed as follows: NF (N*F) ϕ −2.41 br (2.78 br); CF_3 (CF_3*) ϕ −70.81 s (−70.80 s); F_A (F^*_A) ϕ −85.87 d (−86.40 dd); F_B (F^*_B) ϕ −93.36 d (−93.93 d); CF (CF*) ϕ −143.57 s (−147.09 s); $J_{F^*_A-F^*_B} = 187$ Hz; $J_{F^*_A-N^*F} = 9.47$ Hz; $J_{F_A-F_B} = 172$ Hz; $J_{F_A-NF} \simeq 0$; $J_{F^*_B-N^*F} \simeq 0$; $J_{F_B-NF} \simeq 0$. The CI^+ mass spectrum did not show a molecular ion, but the following fragments were found (ratios are for the ^{35}Cl and ^{37}Cl isotopes): *m/e* 196/194 ($C_3F_5N_2Cl^+$, 4.3/13.1%), 182/180 ($CF_3CF_2NClF^+$, 0.6/1.8%), 151/149 ($C_2F_4NCl^+$, 3.1/9.1%), 150 ($C_3F_6^+$, 1.9%), 114 ($C_2F_4N^+$, 12.5%), 101/99 (CF_2NCl^+, 13.3/39.4%), 100 ($C_2F_4^+$, 7.3%), 82/80 ($CFNCl^+$, 10.9/32.7%), and 69 (CF_3^+, 100%). The EI^+ mass spectrum did not show a molecular ion, but the following fragments were found (ratios are for the ^{35}Cl and ^{37}Cl isotopes): *m/e* 196/194 ($C_3F_5N_2Cl^+$, 7.6/22/9%), 182/180 ($CF_3CF_2NClF^+$, 5.5/18.4%), 170/168 ($CF_3CFNClF^+$, 0.4/1.3%), 138/136/134 ($CF_2NCl_2^+$, 0.6/4.3/6.5%), 119 ($C_2F_5^+$, 27.2%), 114 ($C_2F_4N^+$, 3.9%), 101/99 (CF_2NCl^+, 5.1/15.7%), 82/80 ($CFNCl^+$, 10.0/32.9%), 69 (CF_3^+, 100%), 64 (CF_2N^+, 1.5%), and 50 (CF_2^+, 7.3%). Anal. Calcd for $C_3F_7N_2Cl_3$: C, 11.87; F, 43.8; Cl, 35.05; N, 9.23. Found: C, 11.92; F, 44.0; Cl, 34.73; N, 9.24.

Preparation of $FClNCF_2CF_2NCl_2$ (VIII). Into an evacuated 75 mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve were condensed 10 mmol of $FC(=NF)CN$ and 35 mmol of ClF at −196 °C. The cylinder was placed into a slush bath at −78 °C, held at that temperature for ~5 h, and then allowed to warm slowly to ~−10 °C over a 12-h period. Trap-to-trap distillation gave $FClNCF_2CF_2NCl_2$ in ~80% yield as a colorless liquid in the trap at −40 °C. Final purification was done by gas chromatography on a 5 ft OV-1 on Chromosorb P column. The liquid-phase infrared spectrum had bands at 1293 (s), 1195 (vs), 1130 (vs), 1050 (vs), 919 (s), 880 (ms), 840 (ms), 822 (m), 782 (ms), 737 (s), 707 (ms), 692 (ms), 634 (ms), 571 (w), and 493 (w) cm^{-1}. The ^{19}F NMR spectrum for $FClNCF_AF_BCF_CF_DNCl_2$ was analyzed as follows: CF_AF_B, AB pattern with CF_A ϕ −92.68 and CF_B ϕ −97.66; CF_C ϕ −98.63 dd; CF_D ϕ −106.9 d; NF ϕ −5.42; NF* ϕ −5.50 (asymmetric center); $J_{F_A-F_B} = 183$ Hz; $J_{NF-F_A} = 17.3$ Hz; $J_{NF-F_B} \simeq 0$; $J_{F_C-F_D} = 191$ Hz; $J_{F_C-NF} = 36.2$ Hz; $J_{F_D-NF} \simeq 0$. The EI^+ mass spectrum showed a molecular ion at *m/e* 256/254/252 for $M^+ + 4$, $M^+ + 2$, and M^+ (0.5/2.5/2.6%). Other fragments were *m/e* 186/184 ($CF_2CF_2NCl_2^+$, 0.7/1.4%), 138/136/134 ($CF_2NCl_2^+$, 0.9/6.0/8.9%), 114 ($C_2F_4N^+$, 5.9%), 101/99 (CF_2NCl^+, 7.4/23.1%), 100 ($C_2F_4^+$, 5.1%), 88/86/84 (NCl_2^+, 1.9/12.7/21.2%), 82/80 ($CFNCl^+$, 6.2/22.0%), 69 (CF_3^+, 100%), 64 (CF_2N^+, 7.5%), 51/49 (NCl^+, 11.8/32.4%), and 50 (CF_2, 9.2%). Anal. Calcd for $C_2F_5N_2Cl_3$: C, 9.48; F, 37.5; N, 11.05; Cl, 41.97. Found: C, 9.56; F, 37.6; N, 10.93; Cl,.41.86.

Preparation of $[CF_3C(=NF)CF_2N]_2$ (IX). Into an ~200-mL quartz vessel equipped with a Kontes Teflon stopcock was placed 6.5 mmol (1.6 g) of $CF_3C(=NF)CF_2NCl_2$. The flask was cooled to −196 °C and evacuated. The flask was allowed to come to room temperature and photolyzed for 1 h. A yellow liquid and gas were present in the vessel. The vessel was held at −40 °C, and all the volatile materials (mainly Cl_2) were distilled under dynamic vacuum into a liquid-N_2 trap. The photolysis was repeated for another 1 h, and again the volatile materials were distilled off at −40 °C. This procedure was repeated so that the total photolysis time was 5 h. Distillation gave an ~72% yield of $CF_3C(=NF)CF_2N=NCF_2C(=NF)CF_3$ in the trap at −40 °C. Final purification could be achieved by gas chromatography on a 12-ft QF-1 on Chromosorb P column. The liquid-phase infrared spectrum had bands at 1645 (s), 1339 (vs), 1249 (vs), 1194 (vs), 1131 (s), 1018 (ms), 981 (s), 931 (vs), 735 (s), 641 (m), and 503 (m) cm^{-1}. The ^{19}F NMR spectrum showed a broad singlet at ϕ 58.6 (NF), an overlapping set of two triplets at ϕ −64.2 (CF_3), and a six-line pattern of two overlapping quartets at ϕ −87.7 (CF_2), with $J_{CF_2-NF} = 10.98$ Hz and $J_{CF_3-CF_2} = 8.3$ Hz. The EI^+ mass spectrum, obtained at 15 eV, showed the following fragment ions: *m/e* 318 ($M^+ - 2F$, 2.9%), 299 ($M^+ - 3F$, 2.2%), 223 ($CF_3C(=NF)CF_2NNCF^+$, 5.9%), 204 ($CF_3C(=NF)CF_2NNC^+$, 7.3%), 164 ($CF_3C(=NF)CF_2^+$, 4.2%), 126 ($C_3F_4N^+$, 5.4%), and 69 (CF_3^+, 100%). The CI^+ mass spectrum showed a molecular ion, and fragmentation ions of low intensity: *m/e* 357 ($M^+ + 1$, 0.3%), 337 ($M^+ - F$, 0.3%), 223 ($CF_3C(=NF)CF_2NNCF^+$, 0.3%), 204 ($CF_3C(=NF)CF_2NNC^+$, 1.2%), 178 ($CF_3C(=NF)CF_2N^+$, 0.5%), 164 ($CF_3C(=NF)CF_2^+$, 1.9%), 145 ($CF_3C(=NF)CF^+$, 1.3%), 126 ($C_3F_4N^+$, 3.3%), 76 (C_2FN^+, 10.4%), and 69 (CF_3^+, 100%). Anal. Calcd for $C_6F_{12}N_4$: C, 20.22; F, 64.04; N, 15.73. Found: C, 20.22; F, 64.0; N, 15.76.

Preparation of $[CF_3CF(NClF)CF_2N]_2$ (X). The method used to synthesize IX was employed. The total photolysis time was 8 h, starting with 1.89 g (6.2 mmol) of VII. A yellow-green liquid (1.03 g) was found in the trap at −40 °C after trap-to-trap distillation. Gas chromatography (using a 12-ft column of silicone SE-52 on Chromosorb W) showed at least seven compounds to be present. On the basis of the ^{19}F NMR spectrum it is thought that $CF_3CF(NClF)CF_2N=NCF_2CF(NClF)CF_3$ (X) was one of the compounds, but it was not possible to purify the compound in order to obtain elemental analysis data. The ^{19}F NMR spectrum for $(CF_3C^*F(N^*ClF)CF_AF_BN)_2$ was analyzed as follows: NF (N*F) ϕ 2.3 br (5.2 br); CF_3 (CF_3*) ϕ −69.3 s (−70.72 s); F_A (F^*_A) ϕ −76.12 d (−73.44 s); F_B (F^*_B) ϕ −100.0 d (−101.2 s); CF (CF*) ϕ −153.4 s (−154.2 s); $J_{F^*_A-F^*_B} = 132$ Hz; $J_{F_A-F_B} \simeq 0$ Hz. The EI^+ mass spectrum, obtained at 15 eV, did not show a molecular ion but did show a fragment ion of weak intensity due to the loss of ClF, *m/e* 412/410 ($M^+ - ClF$, 0.3/0.5%). Other fragments were as follows: *m/e* 356 ($M^+ - 2ClF$, 4.3%), 264 ($C_5F_{10}N^+$, 7.9%), 214 ($C_4F_8N^+$, 5.7%), 187/185 ($C_3F_6Cl^+$, 6.2/21.4%), 169 ($C_3F_7^+$, 26.2%), 164 ($C_3F_6N^+$, 26.1%), 150 ($C_3F_6^+$, 66.8%), 128 ($C_2F_4N_2^+$, 2.7%), 119 ($C_2F_5^+$, 13.4%), 114 ($C_2F_4N^+$, 12.6%), 87/85 (CF_2Cl^+, 23.9/75.1%), 82/80 ($CNClF^+$, 1.4/3.7%), and 69 (CF_3, 100%). The EI^+ mass spectrum obtained at 70 eV showed only fragments of weak intensity. The CI^+ mass spectrum similarly showed fragments of weak intensity. A fragment ion at *m/e* 357 ($M^+ - 2ClF$, 2.7%) suggests that the loss of chlorine fluoride is the primary mode of fragmentation.

Preparation of $(FClNCF_2CF_2N)_2$ (XI). The method used for IX was employed for XI. The total photolysis time was 7 h. Starting with 1.8 g (7.1 mmol) of VIII, only 0.31 g of a yellow liquid was found in the trap at −40 °C after distillation. Gas chromatography (using a 12-ft column of silicone SE-52 on Chromosorb W) showed at least eight compounds. From this it was possible to isolate a small amount of $FClNCF_2CF_2N=NCF_2CF_2NClF$ (XI) as a yellow liquid. The liquid-phase infrared spectrum showed bands at 1553 (vw), 1446 (vw), 1310 (s), 1217 (vs), 1157 (vs), 1134 (vs), 1043 (s), 920 (s), 883 (m), 846 (ms), 775 (ms), 722 (m), 688 (m), 625 (w), and 555 (w) cm^{-1}. The ^{19}F NMR spectrum for $(FClN^*CF_AF_BCF_CF_DN)_2$ was analyzed as follows: CF_AF_B, AB pattern with CF_A ϕ −103.0 and CF_B ϕ −112.2; CF_C ϕ −105.5 d; CF_D ϕ −105.6 d; NF ϕ −7.98; N*F ϕ −8.07 (asymmetric center); $J_{F_A-F_B} = 199$ Hz; $J_{NF-F_A} = 42.61$; $J_{NF-F_B} = 7.46$; $J_{F_C-F_D} = 13.42$ Hz. The EI^+ mass spectrum obtained at 15 eV did not show a molecular ion. Fragments were as follows: *m/e* 312/310 ($M^+ - ClF$), 0.2/0.4%), 256 ($M^+ - 2ClF$, 1.1%), 164 ($C_3F_6N^+$, 13.5%), 137/135 ($C_2F_4Cl^+$, 1.6/5.5%), 133 ($C_2F_5N^+$, 2.3%), 114 ($C_2F_4N^+$, 17.8%), 87/85 (CF_2Cl^+, 4.2/13.2%), and 69 (CF_3^+, 100%). The CI^+ mass spectrum showed fragment ions of weak intensity but did show the characteristic ion due to the loss of 2 equiv of chlorine fluoride (6.8% intensity).

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