Inorg. Chem. **1993**, *32*, 5011–5020

Perfluorovinylamines: Reactions of the Perfluorovinyl Group with Nucleophiles and Electrophiles

Ashwani Vij, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

Takashi Abe, Haruhiko Fukaya, Eiji Hayashi, and Yoshio Hayakawa

Government Industrial Research Institute, Nagoya Hirate-machi, Kita-ku, Nagoya 462, Japan

Taizo Ono

Daikin MEC Institute, Miyukigaoka 3, Tukuba City 305, Japan

Received June 3, 1993®

The chemistry of acyclic and heterocyclic perfluoro-*N*-vinylamines has been investigated extensively for the first time. The reaction of these compounds with electrophiles is equally facile when compared to those with nucleophiles even under very mild conditions. With nitrogen based nucleophiles such as ammonia, methylamine, and 2,2,2-trifluoroethylamine, R_fCHFCN and $R_fCHFCF{=}NR$ [$R_f = \overline{CF_2CF_2CF_2CF_2N}$ or $\overline{CF_2CF_2OCF_2CF_2N}$ and R = CH_3 or CH_2CF_3] are obtained, respectively. Formation of β-substituted perfluorovinylamines i.e. $R_fCF{=}CFR$ [$R_f = \overline{CF_2CF_2CF_2CF_2N}$ or $\overline{CF_2CF_2OCF_2CF_2N}$ and R = CH_3, n-C_4H_9 or $N(CH_3)_2$] is achieved using alkyllithium or (dimethylamino)trimethylsilane reagents. Some of these derivatives have good potential as monomers for the little known perfluorovinylamine copolymers. Reaction with electrophilic reagents such as $ClOSO_2F$, ClF, and SF_5OCl results in bidirectional addition to form isomers of the type R_fCFXCF_2Cl (I) and $R_fCFClCF_2X$ (II) [$R_f = \overline{CF_2CF_2CF_2CF_2N}$, $\overline{CF_2CF_2OCF_2CF_2N}$, $\overline{CF_2CF_2CF_2CF_2CF_2N}$ or $(CF_3)_2N$; X = F, OSO_2F or OSF_5]. However, in some cases only isomer I is obtained, e.g., $\overline{CF_2CF_2CF_2CF_2CF_2N}CF(OSO_2F)CF_2Cl$, from the reaction with $ClOSO_2F$ as an addition product. When CF_3OF is added across these perfluorovinylamines, a single addition isomer $R_fCF_2CF_2OCF_3$ is formed. With $(CF_3)_3COCl$, complete reversal of addition is observed on reaction with perfluorovinylpyrrolidine vis-à-vis perfluorovinylmorpholine. Although no reaction is observed thermally, photolytic reactions with SF_5Cl and $(CF_3)_2NCl$ give $R_fNCFXCF_2Cl$ [$R_f = \overline{CF_2CF_2CF_2CF_2N}$ or $\overline{CF_2CF_2OCF_2CF_2N}$; X = $N(CF_3)_2$ or SF_5]. These derivatives are characterized by IR, NMR, and mass spectra and elemental analyses.

Introduction

Perfluorovinylamines comprise an interesting class of compounds. A survey of the literature reveals that these compounds have not received much attention as reaction precursors, primarily due to the lack of facile synthetic routes. However, electrochemical fluorination techniques provide a convenient high-yield synthesis of the precursors to these vinylamines.[1] Methods reported for the synthesis of three perfluorovinylamines known prior to those reported by Abe,[2] i.e., perfluoro(*N*,*N*-dimethylvinyl)amine,[3,4] perfluorovinylpiperidine,[5] and perfluorovinylmorpholine,[6] are not convenient. They involve the addition of the $(CF_3)_2N$ radical to an appropriate olefin followed by dehalogenation[3] and the flow pyrolysis of perfluorocyclobutylamines at 600–750 °C with a specific contact time.[3,5,6]

The only chemistry reported for these perfluorovinylamines is bromination and hydrobromination under photolytic conditions.[3,5,6] Their interaction with nucleophiles has not been investigated. Although anionic hydrobromination is quite facile in the case of *N*,*N*-bis(trifluoromethyl)vinylamine,[7] its perfluorovinyl analogue is recovered unreacted after 14 days under similar conditions.[3] Static and flow pyrolytic rearrangement of $(CF_3)_2NCF{=}CF_2$ results in isomerization to $CF_3CF_2CF{=}NCF_3$ and C_2F_6.[7,8] In the presence of toluene, CF_3H is also formed as well as other decomposition products, such as COF_2, CF_3NCO and SiF_4. Copolymerization of $(CF_3)_2NCF{=}CF_2$ with $CH_2{=}CHF$ in the presence of N_2F_2 is reported to give a product which can be pressed to give a transparent film.[4] Studies of the reaction of some perfluorovinylmorpholine chloro/bromo derivatives with chlorine(I) fluorosulfate are reported.[9]

Our interest in the chemistry of perfluorovinylamines was sparked by the industrial and commerical applications of perfluoropoly ethers prepared by the copolymerization of perfluorovinyl ethers with tetrafluoroethylene.[10] A recent report suggests that perfluoropoly ethers useful as lubricants, break down when subjected to a high-energy, low-current density electron beam resulting in the formation of corrosive products, such as COF_2, which cause degradation of materials.[11] The possible utilization of vinylamine derivatives in similar roles has not been examined.

® Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Abe, T.; Hayashi, E.; Shimizu, T. *Chem. Lett.* **1989**, 905.

(2) Abe, T.; Hayashi, E. *Chem. Lett.* **1988**, 1887.

(3) Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1968**, 398.

(4) Fawcett, F. S. U.S. Pat. 3311599, **1967**.

(5) Banks, R. E.; Mullen, K.; Williamson, G. E. *J. Chem. Soc. C* **1968**, 2608.

(6) Banks, R. E.; Parker, A. J.; Sharp, M. J.; Smith, G. F. *J. Chem. Soc., Perkin Trans. 1* **1973**, 5.

(7) Alexander, E. S.; Haszeldine, R. N.; Newland, M. J.; Tipping, A. E. *J. Chem. Soc. C* **1968**, 796.

(8) Fleming, G. L.; Haszeldine, R. N.; McAllister, J. R.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1633.

(9) Kirchmeier, R. L.; Abe, T.; Hayashi, E.; Fukaya, H.; Hayakawa, Y.; Ono, T. *J. Fluorine Chem.*, in press.

(10) *Encyclopedia of Chemical Technology*, 3rd ed.; Interscience: New York, 1980; Vol. 11, p 1.

0020-1669/93/1332-5011$04.00/0

The ready availability of the starting materials, simplicity of the high-yield synthetic approach, and the ease of scaling the reaction up are the main advantages of the electrochemical method for the preparation of perfluorovinylamine precursors and subsequently the perfluorovinylamines. Consequently, we carried out the first extensive investigation of the chemistry of some representative perfluorovinylamines with a variety of nucleophilic, electrophilic and free radical substrates. Some of the unsaturated derivatives and perfluorinated tertiary amines obtained during this study have good potential in polymer chemistry as well as important properties for use as blood or CFC substitutes.

Results and Discussion

Pyrolysis of alkali metal perfluorocarboxylates or of perfluoro-2-alkoxypropionic acid is an efficient method for the preparation of perfluoroalkenes and perfluorovinyl ethers,[10] respectively. This method is used to synthesize perfluorovinylamines[1] by the thermal decarboxylation of alkali metal salts of perfluoro(3-dialkylaminopropionic) acids.

$$RCH_2CH_2COCl{\cdot}HCl \text{ or } RCH_2CH_2COOCH_3 \xrightarrow{\text{ECF}} R_fCF_2CF_2COF \xrightarrow[\text{ii. evaporate to dryness}]{\text{i. aqueous KOH}} R_fCF_2CF_2COO^-K^+ \xrightarrow[-CO_2,\,-KF]{\Delta} R_fCF{=}CF_2$$

$$R_f = \overline{CF_2(CF_2)_2CF_2N}\ (\mathbf{A}),\ \overline{CF_2CF_2OCF_2CF_2N}\ (\mathbf{B}),\ (CF_3)_2N\ (\mathbf{C}),\ \overline{CF_2(CF_2)_3CF_2N}\ (\mathbf{D})$$

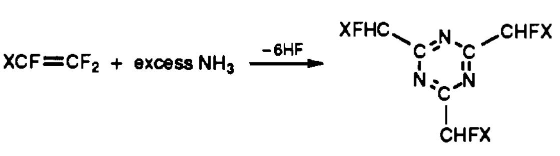
In this study the reactivity of the perfluorovinyl group in these compounds with some electrophilic/nucleophilic reagents is compared to the reactivity of fluoroalkenes and perfluorovinyl ethers with similar reagents.

Reaction with Nucleophiles. Perfluorovinylpyrrolidine (**A**) and perfluorovinylmorpholine (**B**) react with a variety of nitrogen and carbon nucleophiles to give monomeric nitriles, azaalkenes, or β-substituted perfluorovinylamines under very mild conditions. In each of these reactions, the β-difluoromethylene group is the reactive site. Reaction of **A** and **B** with a 2-fold excess of ammonia results in the formation of the corresponding nitriles in good yields via an addition–elimination process. A similar reaction is reported for the preparation of α-hydroperfluoropropionitrile although it involves a less convenient synthetic route and gives the desired compound in lower yields.[12]

$$R_fCF{=}CF_2 + \text{excess } NH_3 \xrightarrow{-2HF} R_fCHFCN \qquad R_f = \mathbf{A}\ (\mathbf{1});\ \mathbf{B}\ (\mathbf{2})$$

The presence of the CHF doublet in the ^{1}H and ^{19}F NMR indicates that nucleophilic attack of NH_3 occurs at $=CF_2$ of the perfluorovinyl group while the appearance of M^+ ions in the mass spectra and $\nu_{C\equiv N}$ at $\sim$2267 cm^{-1} in the IR spectra of **1** and **2** confirm the monomeric nature of these derivatives.

However, the analogous reactions of NH_3 with $CF_3OCF{=}CF_2$ and C_2F_4 do not give isolable nitriles since the intermediate undergoes trimerization to form 2,4,6-tris[fluoro(trifluoromethoxy)methyl]triazene and tris[difluoromethyl]triazene, respectively.[13]



(X = F or OCF_3)

The ^{19}F NMR spectra are very useful for characterization of the perfluorovinylamines and their derivatives. In cyclic compounds such as **A** and **B**, $-CF_2OCF_2-$, $-CF_2NCF_2-$, and $-CF_2CF_2-$ fluorine atoms occupy axial or equatorial positions and, therefore, appear as AB type quartets at δ $\sim$−85, $\sim$−93, and $\sim$−133 ppm, respectively. There are further complications which arise from long-range F–F couplings. The *gem*-difluoro couplings are in the range 120–250 Hz. The CHF region generally appears as a doublet of pentets by coupling to the nearest ring fluorines with $J_{HF} \approx 47$ Hz and $J_{FF} \approx 10$ Hz.

Similarly, the vinylic difluoromethylene group is attacked by primary amines which results in the formation of azaalkenes.

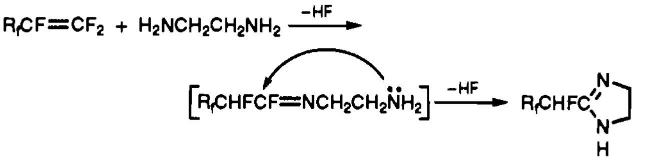
$$R_fCF{=}CF_2 + H_2NR \xrightarrow{-HF} R_fCHFCF{=}NR$$

$$R_f = \mathbf{A};\ R = CH_3\ (\mathbf{3}),\quad R = CH_2CF_3\ (\mathbf{4})$$

$$R_f = \mathbf{B};\ R = CH_3\ (\mathbf{5}),\quad R = CH_2CF_3\ (\mathbf{6})$$

Noted in the IR spectra of these compounds are bands at 1760–1775 cm^{-1} attributed to $\nu_{C=N}$. In the ^{19}F NMR spectrum, the CF═N fluorine resonance appears as a doublet at δ $\sim$−40 ppm. The ^{19}F NMR spectrum of **3** shows an interesting 14-line pattern due to the CHF group. This is simulated theoretically to give a doublet of doublet of pentets (ddp) pattern that is obtained by assuming values for the coupling constants of the CHF fluorine atom to the geminal proton, vicinal fluorine atom and the nearest ring $[N(CF_2)_2]$ fluorine atoms. The doublet of pentets (dp) observed for the CF═N fluorine atom is consistent with this simulation.

In an attempt to form diazaalkenes, an excess of the perfluorovinylamine is reacted with ethylene diamine. The ^{19}F NMR spectrum of the product, however, does not show any resonance assignable to the CF═N fluorine atom. This suggests that the intramolecular cyclization of the intermediate azaalkene with concomitant loss of both terminal vinylic fluorines is favored over formation of a diazaalkene to give compounds which contain perfluorinated and nonfluorinated heterocyclic rings on the same carbon atom, viz.



R_f = **A** (**7**), **B** (**8**)

The formation of **7** and **8** is supported by the appearance of M^+ and $[M^+ - \overline{C{=}NCH_2CH_2NH}]$ ions in the mass spectra, and preliminary X-ray crystallographic data in case of **8**. These compounds have potential as monomers for the formation of amphiphilic fluorinated polymers similar to those reported by the cationic ring opening polymerization of 2-oxazolines and 2-oxazines.[14]

Reactions of **A** and **B** with alkyllithium reagents, such as CH_3Li and n-C_4H_9Li, in diethyl ether/hexane, and dimethylaminotrimethylsilane without solvent or fluoride ion catalyst, yield the corresponding β-substituted perfluorovinylamine derivatives:

---

(11) Pacansky, J.; Waltman, R. J. Presented at the American Chemical Society Eleventh Winter Fluorine Symposium, St. Petersburg, FL, 1993; Abstr. No. 9.

(12) Knunyants, I. L.; German, L. S.; Dyatkin, B. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1956**, 1353.

(13) Tumanova, A. V.; Gubanov, V. A.; Dalgopol'skii, I. M. *Zh. Obshch. Khim.* **1965**, *35*, 399. Henne, A. L.; Pelley, R. L. *J. Am. Chem. Soc.* **1952**, *74*, 1426.

(14) Parada, J. M. R. Presented at the American Chemical Society Eleventh Winter Fluorine Symposium, St. Petersburg, FL, 1993; Abstr. No. 60.

$$R_fCF{=}CF_2 + RLi \xrightarrow[Et_2O/hexane]{-LiF} R_fCF{=}CFR$$

$$R_f = \mathbf{A};\ R = CH_3\ (\mathbf{9}),$$
$$R = C_4H_9\ (\mathbf{10})$$
$$R_f = \mathbf{B};\ R = CH_3\ (\mathbf{11}),$$
$$R = C_4H_9\ (\mathbf{12})$$

$$R_fCF{=}CF_2 + (CH_3)_3SiN(CH_3)_2 \xrightarrow{-(CH_3)_3SiF} R_fCF{=}CFN(CH_3)_2$$
$$R_f = \mathbf{A}\ (\mathbf{13}),\ \mathbf{B}\ (\mathbf{14})$$

These compounds are colorless liquids and the dimethylamino derivatives (**13**, **14**) are moisture sensitive. The IR spectra of the alkyl derivatives (**9**–**12**) show a characteristic weak to very weak band at 1765–1780 cm^{-1} assigned to $\nu_{C=C}$. The ^{19}F NMR spectra are most useful for structural assignments in these compounds. The large coupling constant value (110–134 Hz) for the olefinic fluorine atoms in these derivatives is greater than the range characteristic of the trans-isomer.[15,16] These trans fluorine atoms show different types of AB patterns. For example, the methyl derivatives (**9**,**11**) show an AB pattern of 8 and 14 lines for the two olefinic fluorines while for the *n*-butyl derivatives (**10**,**12**), these appear as 7 and 13 lines, respectively. Simulation of the latter spectra suggests that the eight lines arise from couplings of the α-fluorine atom with the vicinal CH$_3$ protons ($J_{HF} \approx 2.5$ Hz) and ring [–CF$_2$NCF$_2$–] fluorine atoms to give the quartet of pentets (qp) pattern. Similar couplings exist for the β-fluorine atom but the 14 lines arise due to the larger coupling constant ($J_{HF} \approx 16.8$ Hz) of the geminal fluorine with methyl protons. These coupling constant values are also found from the ^{1}H NMR where a doublet of doublets (dd) is observed for the methyl protons via coupling to the α- and β-fluorine atoms. These are in good agreement with those reported previously.[17,18] The triplet of pentets pattern from the seven and thirteen line spectra of **10** and **12** can also be explained on a similar basis with a geminal fluorine-methylene proton coupling on the order of ~20 Hz. The ^{1}H NMR spectra of the olefinic methylene group shows a twelve line triplet of doublets of doublets (tdd) pattern which can be simulated by considering couplings from vicinal CH$_2$ and F and geminal F nuclei. The ^{19}F NMR spectra shows that a trace amount of the cis product is also formed.

Reaction with Electrophiles. The only successful electrophilic addition reaction reported is the addition of chlorine(I) fluorosulfate to perfluorovinylmorpholine.[9] Attempted electrophilic hydrobromination reactions of some perfluorovinylamines are unsuccessful although hydrobromination is accomplished photolytically.[3,6] In this study, all electrophilic reactions are carried out under very mild conditions.

A mixture of addition isomers in varying stoichiometries (Table I) is obtained when perfluorovinylamines are reacted with electrophilic reagents i.e., ClF, ClOSO$_2$F, and ClOSF$_5$, where the chlorine atom is known to be positive in character.[19] The two isomers are easily identified by their ^{19}F NMR spectra where the CF$_2$Cl (isomer I) fluorine atoms appear at –60 to –70 ppm while CF$_2$ fluorine atoms for the other isomer CF$_2$X (isomer II) are in the –80 to –90 ppm region. The formation of addition isomers is observed during the reaction of CFCl=CF$_2$ with ClOSO$_2$F,[20] BrOSO$_2$F,[21] and interhalogens[22,23] and is accounted for by anelectrophilic mechanism.[19,20,24] Addition of ClF to the perfluorovinylamines results in the formation of isomer I as the major product. With the exception of perfluorovinylpyrrolidine, regioselectivity increases with heterocyclic ring size. Chlorine(I) fluorosulfate adds bidirectionally to all of the perfluorovinylamines. While perfluorovinylpyrrolidine forms approximately equimolar amounts of both isomers (**26**, **27**), perfluorovinylpiperidine forms only a single addition product (**28**). The latter substrates behaves similarly to CF$_3$OCF=CF$_2$ in reactivity toward ClOSO$_2$F.[25] As is the case with perfluorovinylmorpholine,[9] no bis(fluorosulfate) adduct is isolated in these reactions.

Table I. Addition Reactions of Perfluorovinylamines with Electrophilic Reagents

$$R_fCF{=}CF_2 + ClX \rightarrow \underset{\mathbf{I}}{R_fCFXCF_2Cl} + \underset{\mathbf{II}}{R_fCFClCF_2X}$$

perfluoroalkyl group (R$_f$)	X	ref isomer ratio[a] I	II
(CF$_3$)$_2$N	F	2.22	1.0
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$[b]	F	1.0	2.0
$\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$	F	5.4	1.0
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$	F	12.8	1.0
(CF$_3$)$_2$N	OSO$_2$F	4.65	1.0
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$	OSO$_2$F	1.01	1.0
$\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$[c]	OSO$_2$F	6.55	1.0
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$	OSO$_2$F	1.0	0
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$	OSF$_5$	1.0	1.6
$\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$	OSF$_5$	1.0	1.3
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$	OC(CF$_3$)$_3$	~1.0	trace
$\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$	OC(CF$_3$)$_3$	trace	~1.0

[a] Determined from ^{19}F NMR. [b] Addition of chlorine is also observed to give the 1:1 dichloro adduct (16.5% yield; total yield = 77.7%). [c] Reference 9, addition of two OSO$_2$F groups observed (yield 2%, total yield = 85%).

The addition of hypohalites R$_f$OX (X = F, Cl) takes place in the absence of a catalyst and shows an interesting addition pattern. A single isomer is (**33**–**36**) obtained when CF$_3$OF is reacted with all four perfluorovinylamines. This is in contrast to the addition reactions of CF$_3$OF with olefins, where a free radical mechanism is proposed to account for its poor regioselectivity.[26] The reaction of CF$_3$OF with perfluorovinylpyrrolidine gives only a ~6% yield of the addition product (**34**). The mechanism for the formation of other products in this reaction, i.e., COF$_2$ and CF$_4$, is not currently known. Interestingly, CF$_3$OCl adds to perfluorovinylpyrrolidine to give a single major isomer, but perfluorovinylmorpholine does not form a 1:1 adduct under similar conditions. The addition of (CF$_3$)$_3$COCl to perfluorovinylpyrrolidine and perfluorovinylmorpholine is most intriguing. While the former yields isomer I (**38**) exclusively, the latter undergoes reversal of addition yielding isomer **II** (**39**). These are identified from the multiplicity of the (CF$_3$)$_3$CO peak in the NMR spectrum and the

---

(15) Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; McDonald and Company: London, 1970; pp 232–235.

(16) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon Press: New York, 1977.

(17) Reilly, C. A. *J. Chem. Phys.* **1962**, *37*, 456. Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; McDonald and Company: London 1970; pp 187–193.

(18) DeWolf, M. Y.; Baldeschweiler, J. D. *J. Mol. Spectrosc.* **1964**, *13*, 344.

(19) Schack, C. J.; Christie, K. O. *Isr. J. Chem.* **1978**, *17*, 20.

(20) Fokin, A. V.; Studnev, Y. N.; Kuznetsova, L. D.; Rud, V. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 471.

(21) Earl, B. L.; Hill, B. K.; Shreeve, J. M. *Inorg. Chem.* **1966**, *5*, 2184.

(22) Dyatkin, B. L.; Mochalina, E. P.; Knunyants, I. L. *J. Fluorine Chem.* **1969**, *3*, 45.

(23) Dyatkin, B. L.; Knunyants, I. L. *Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva* **1970**, *15*, 5.

(24) Fokin, A. V.; Studnev, Y. N.; Kuznetsova, L. D.; Krotovich, I. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 649.

(25) Fokin, A. V.; Studnev, Y. N.; Rapkin, A. I.; Ngem, N. C.; Zagorevskii, D. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1572.

(26) Johri, K. K.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 242.

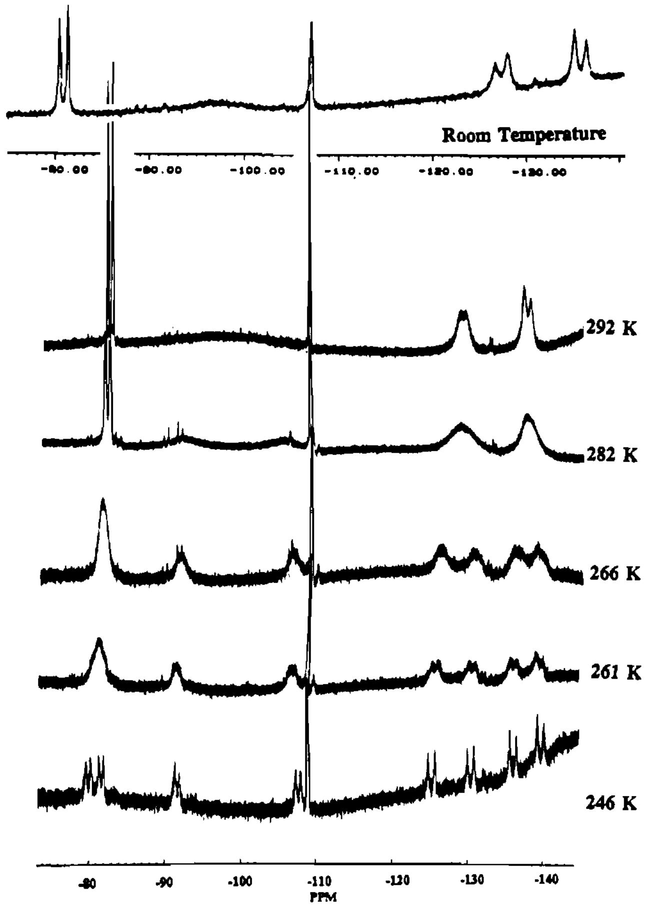


Figure 1. Variable-temperature ^{19}F NMR of $\overline{CF_2CF_2CF_2CF_2N}CF[OC(CF_3)_3]CF_2Cl$ in the Ring Region.

position of the CF_2Cl fluorine resonances. Since electronic factors are expected to be the same in these two perfluorovinylamines, supported by the similar position of $CF{=}CF_2$ resonances in the ^{19}F NMR spectra, the additions seem to be sterically controlled. Since these reactions are carried out under similar conditions, external factors are excluded from the reaction mechanism.

In the room temperature ^{19}F NMR spectrum of (**38**) a broad hump is observed at −98.5 with a line width of ~1 kHz (Figure 1). When the temperature is lowered from 292 to 231 K, coalescence–decoalescence effects for these ring resonances are observed. At 231 K, the compound begins to precipitate from solution. Decoalescence of the broad hump into two peaks is observed at 282 K while peaks due to the $-CF_2CF_2-$ ring fluorine atoms coalesce. Further lowering of the temperature to 246 K causes complete decoalescence of all the ring fluorine atoms to give eight AB type doublets. Estimation[27] of rate data (k_c) and free energy of activation for the exchange (ΔG^{*}) at coalescence temperature (T_c) is determined from Bloch and Eyring equations. The ΔG^{*} and k_c values at 292 and 266 K for the $-CF_2NCF_2-$ group are found to be 11.7 kcal mol^{-1} and ~10 515 (broad hump) and 1281 s^{-1}, respectively. For the $-CF_2CF_2-$ fluorines, ΔG^{*} and k_c at 282 K are 11.9 and 12.1 kcal mol^{-1} and 3419 and 2371 s^{-1}, respectively. These values suggest that the dynamic processes involved are slow.

At present it is not clear that the addition reactions of electrophiles with these perfluorovinylamines are purely electrophilic in nature. A free radical mechanism cannot be ruled out. The chemistry of perfluorovinylamines and perfluorovinylethers show somewhat different behavior in reactions with $ClOSO_2F$ where only a single addition isomer is isolated with the latter. However, both perfluorovinylamines and perfluorovinylethers show reversal in the mode of addition of hypochlorites. Since both of these reactions are presumably electrophilic in nature, attack of the chloronium ion is expected on the same carbon center in both the cases. The reasons for anomalies observed are presently under investigation in our laboratories.

Reaction with Free Radicals. Thermal insertion of the perfluorovinylamines into the N–Cl and S–Cl bond of $(CF_3)_2NCl$ and SF_5Cl is unsuccessful. However, photolysis in a quartz vessel at 3000 Å results in the formation of 1:1 adducts. In addition to the desired compound, a chlorine adduct, S_2F_{10} or $(CF_3)_4N_2$, and an unidentified nonvolatile residue are also obtained. In these reactions, chlorine attacks the β-difluoromethylene group.

$$R_fCF{=}CF_2 + ClX \xrightarrow[\substack{3000\,\text{Å}\\ \text{quartz}}]{h\nu} R_f\dot{C}FCF_2Cl \xrightarrow{X^{\bullet}} R_fCFXCF_2Cl$$

$$X = SF_5;\ R_f = \mathbf{A}\ (\mathbf{40});\ \mathbf{B}\ (\mathbf{41})$$

$$X = N(CF_3)_2;\ R_f = \mathbf{A}\ (\mathbf{42});\ \mathbf{B}\ (\mathbf{43})$$

This effect is also observed in the addition reaction of SF_5Cl with chlorotrifluoroethylene.[28] Assuming a radical electrophilicity in the order $Cl^{\bullet} > SF_5^{\bullet} > (CF_3)_2N^{\bullet}$, initial attack is anticipated on the vinylic CF_2 group. Analogous reactions of $(CF_3)_2NCl$ with $CFCl{=}CF_2$ give a complex mixture of products from which the 1:1 adduct can not be isolated.[29] However, isolation of the desired compound in this work suggests that radical additions take place in a more controlled manner.

For the first time, the reactions of the perfluorovinylamines with nucleophiles show that the β-difluorocarbon is the center of nucleophilic attack. This observation is similar to that for fluoroalkenes and perfluorovinylethers.[12] The intermediate formed from the nucleophilic attack generates the carbanion at the α-position which may be stabilized by the inductive effect of the neighboring CF_2 and perfluoroamino groups and, probably, the anomeric effect of the heterocyclic ring.[30] The reactivity of the perfluorovinylamines may be compared to perfluorovinylethers since both contain a lone pair bearing heteroatom on the perfluorovinyl group. Gard *et al.*[31] suggest that electron mobilization from an oxygen lone pair into the olefinic π-electron cloud induces a partial negative charge on the β-difluorocarbon, thereby making it susceptible to attack by electrophiles like SO_3. We find that perfluorovinylamines behave similarly,[32] but this argument would contradict the observed nucleophilic attack on the same carbon, as observed in the case of perfluorovinylethers.[12]

Conclusion

Perfluorovinylamines have been found to be a interesting class of compounds with a very reactive perfluorovinyl group. The β-difluoromethylene carbon is the center for nucleophilic attack resulting in addition-elimination products, including formation of new β-substituted perfluorovinylamines. The perfluorovinyl group also undergoes addition reactions with a variety of electrophilic reagents under mild conditions in the absence of a catalyst.

Experimental Section

Materials. The reagents, NH_3, CH_3Li, n-C_4H_9Li, CH_3NH_2, and $(CH_3)_3SiN(CH_3)_2$ (Aldrich Chemical Co. Inc.); $CF_3CH_2NH_2$ (PCR); $H_2NCH_2CH_2NH_2$ (J. T. Baker); and SF_4, COF_2, and ClF (Atochem North America) are purchased as indicated and used as received. $(CF_3)_3$-

---

(27) Oki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers Inc.: New York, 1985.

(28) Case, J. R.; Ray, N. H.; Roberts, H. L. *J. Chem. Soc.* **1961**, 2070.

(29) Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc.* **1965**, 6141.

(30) Gilchrist, T. L. *Heterocyclic Chemistry*, 2nd ed.; Longman Scientific and Technical: London, 1992, 47–53 and references therein.

(31) Mohtasham, J.; Behr, F. E.; Gard, G. L. *J. Fluorine Chem.* **1990**, *49*, 349.

(32) Vij, A.; Kirchmeier, R. L.; Shreeve, J. M. To be submitted for publication.

COCl and $(CF_3)_2NCl$ are prepared by the reaction of ClF with $KOC(CF_3)_3$[33,34] and $CF_3N{=}CF_2$.[35] CF_3OF,[36] CF_3OCl,[37] SF_5OCl,[37] SF_5Cl,[38] and perfluorovinylamines,[1] i.e., $(CF_3)_2NCF{=}CF_2$, $CF_2CF_2CF_2CF_2NCF{=}CF_2$, $CF_2CF_2OCF_2CF_2NCF{=}CF_2$ and $CF_2CF_2CF_2CF_2CF_2NCF{=}CF_2$, are prepared by known methods.

General Procedures. A conventional vacuum system, consisting of a Pyrex glass vacuum line fitted with Teflon needle stopcocks (ChemGlass) and equipped with Heise Bourdon tube and Televac thermocouple gauges, is used to handle gases and volatile liquids. Standard *PVT* techniques or direct weighing are used to quantitate starting materials or products. Fractional condensation (trap-to-trap distillation) or gas chromatography is used for the purification of products. The products are handled in a dry nitrogen atmosphere since some of them are moisture sensitive. Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR or Hitachi EPI-G3 spectrometer with a 10-cm glass cell equipped with KBr windows. ^1H and ^{19}F NMR spectra are obtained on a Bruker AC200/AC300 FT-NMR or Hitachi R-90F spectrometer using $CDCl_3$ as a solvent. Chemical shifts for ^1H and ^{19}F NMR spectra are reported with respect to Me_4Si and $CFCl_3$, respectively. Mass spectra are obtained with a Varian VG 7070 HS or Shimadzu GC/MS Model 7000 mass spectrometer. Peak assignments of the chlorine-containing fragments are based on the ^{35}Cl isotope. A Gasukuro LL-75 modified gas chromatograph is used for semipreparative gas chromatography by using 10-mm-diameter stainless steel columns packed with 25% Kel-F 90 on Chromosorb PAW. Theoretical NMR spectra are simulated using the PMR program from Sarena software on an IBM-386 compatible microcomputer. The chemical shifts of the AB type ^{19}F NMR spectra are calculated by known procedures.[39,40] Elemental analyses were performed by Beller Microanalytisches Laboratorium, Göttingen, Germany. Isomer ratios were determined by NMR. Photochemical reactions are conducted in a Rayonet ultraviolet reactor with 3000-Å lamps using a quartz vessel.

Reaction with Nucleophiles. Preparation of $CF_2CF_2CF_2CF_2NCHFC{\equiv}N$ (1) and $CF_2CF_2OCF_2CF_2NCHFC{\equiv}N$ (2). Into a 50-mL Pyrex glass reactor fitted with a Teflon stopcock is condensed anhydrous ammonia (3.1–3.2 mmol) onto 1 mmol of the perfluorovinylamine (**A** or **B**) at −196 °C. The reaction vessel is allowed to warm to 25 °C over 12 h. The products are fractionated by trap-to-trap distillation.

Properties of $CF_2CF_2CF_2CF_2NCHFC{\equiv}N$ (1). Compound **1** is isolated in a trap cooled to −30 °C after having passed −10 °C. It was obtained as a colorless liquid in 71% yield. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2983 w, br, 2268 mw ($\nu_{C\equiv N}$), 1422 s, 1397 ms, 1338 vs, 1276 vs, 1225 vs, 1176 vs, 1143, s, 1087 s, 1052, s, 1020 m, 983 vs, 938 m, 849 m, 711 mw, 677 w, 639 vw, 606 w, 580 mw, 544 m, 459 mw. NMR [$CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}NCH^EF^FC{\equiv}N$]: ^{19}F, δ −90.3 (A, AB m), −94.3 (B, AB m), −131 (C, AB m), −134.7 (D, AB m), −138.9 (f, dp); ^1H, δ 6.22 (E, d). J_{AB} = 171 Hz, J_{CD} = 253 Hz, J_{EF} = 48.2 Hz, $J_{(AB)F}$ = 10.1 Hz. MS CI [*m/e* (species), intensity]: 273 (MH^+), 5.7; 253 ($M^+ - F$), 22.2; 247 ($MH^+ - CN$), 5.2; 246 ($M^+ - CN$), 100; 235 ($MH^+ - 2F$), 1.7; 228 ($MH^+ - F - CN$), 8.6; 214 ($C_4F_8N^+$), 1.1; 196 ($C_4F_7HN^+$), 6.9; 177 ($C_4F_6HN^+$), 4.0; 176 ($C_4F_6N^+$), 7.1; 145 ($C_3F_5N^+$), 2.3; 131 ($C_3F_5^+$), 3.4; 119 ($C_2F_5^+$), 3.8; 114 ($C_2F_4N^+$), 2.3; 100 ($C_2F_4^+$), 11.6; 96 ($C_2F_3HN^+$), 16.2; 95 ($C_2F_3N^+$), 8.6; 83 (CF_3N^+), 9.5; 81 ($C_2F_3^+$), 11.5; 69 (CF_3^+), 26.9; 58 (C_2FHN^+), 3.6. Anal. Calcd for $C_6F_9HN_2$: C, 26.47; F, 62.8; H, 0.37. Found: C, 26.62; F, 62.7; H, 0.43.

Properties of $CF_2CF_2OCF_2CF_2NCHFC{\equiv}N$ (2). Compound **2** is found in a trap cooled to −30 °C having passed −10 °C. This colorless liquid is obtained in 73% yield. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 3011 vw, br, 2267 mw ($\nu_{C\equiv N}$), 1422 ms, 1330 sh, 1308 vs, 1242 sh, 1230 vs, 1176 s, 1146 vs, 1088 ms, 1070 ms, 1046 m, 974 ms, 932 vw, 886 ms, 801 mw, 718 mw, 686 mw, 630 mw, 602 mw, 566 w, 488 mw, 414 mw. NMR [$CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}NCH^EF^FC{\equiv}N$]: ^{19}F, δ −86.9 (C, AB m), −88.3 (D, AB m), −94.1 (A, AB m), −95.3 (B, AB m), −143.2 (F, dp); ^1H, δ 6.39 (E, d). J_{AB} = 195 Hz, J_{CD} = 153 Hz, J_{EF} = 46 Hz, $J_{(AB)F}$ = 9.2 Hz. MS CI [*m/e* (species), intensity]: 289 (MH^+), 4.7; 269 ($M^+ - F$), 25.8; 263 ($MH^+ - CN$), 5.8; 262 ($M^+ - CN$), 100; 251 ($MH^+ - 2F$), 0.8; 244 ($MH^+ - F - CN$), 3.4; 230 ($C_4F_8NO^+$), 0.3; 212 ($C_4F_7HNO^+$), 3.0; 192 ($C_4F_6NO^+$), 6.0; 178 ($C_4F_6O^+$), 1.1; 164 ($C_3F_6N^+$), 5.4; 147 ($C_3F_5O^+$), 2.7; 145 ($C_3F_5N^+$), 4.1; 131 ($C_3F_5^+$), 4.1; 119 ($C_2F_5^+$), 12.0; 114 ($C_2F_4N^+$), 11.8; 100 ($C_2F_4^+$), 60.4; 96 ($C_2F_3HN^+$), 14.3; 95 ($C_2F_3N^+$), 12.8; 83 (CF_3N^+), 6.8; 81 ($C_2F_3^+$), 9.6; 69 (CF_3^+), 23.6; 58 (C_2FHN^+), 14.2. Anal. Calcd for $C_6F_9HN_2O$: C, 25.01; F, 59.3; H, 0.35. Found: C, 25.16; F, 58.3; H, 0.37.

Preparation of $CF_2CF_2CF_2CF_2NCHFCF{=}NR$ and $CF_2CF_2OCF_2CF_2NCHFCF{=}NR$ [R = CH_3 or CH_2CF_3]. Into a reaction flask, fitted with a Kontes Teflon stopcock, is condensed ~1 mmol of the perfluorovinylamine (**A** or **B**) and 2–2.1 mmol of the primary amine at −196 °C. The reaction mixture is allowed to warm slowly to 25 °C. The desired product is isolated as a slightly volatile liquid from a solidified reaction mixture by trap-to-trap distillation. These derivatives are moisture sensitive and require handling under an inert atmosphere.

Properties of $CF_2CF_2CF_2CF_2NCHFCF{=}NCH_3$ (3). Compound **3** is isolated as a colorless liquid in 78% yield in a trap cooled to −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2957 w, 2934 w, 2868 w, 1777 m/1760 ms ($\nu_{C=N}$), 1424 m, 1398 mw, 1342 s, 1278 vs, 1224 vs, 1167 s, 1141 ms, 1098 m, 1069 ms, 1017 w, 995 m, 966 s, 906 vw, 820 w, 736 m, 703 mw, 675 w, 640 w, 573 mw, 542 mw, 481 mw. NMR [$CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}NCH^EF^FCF^G{=}NCH_3^H$]: ^{19}F, δ −44.2 (G, dp), −92.0 (A, AB m), −92.1 (B, AB m), −132.1 (C, AB m), −133.4 (D, AB m), −151.4 (F, ddp); ^1H, δ 3.17 (H, s), 5.94 (E, d). J_{AB} = 181 Hz, J_{CD} = 253 Hz, $J_{(AB)G}$ = ~4 Hz, $J_{(AB)F}$ = 9.9 Hz, J_{FG} = 23.7 Hz, J_{EF} = 47.4 Hz. MS CI [*m/e* (species), intensity]: 307 (MH^+), 0.4; 305 ($M^+ - H$), 1.4; 287 ($M^+ - F$), 39.0; 268 ($M^+ - 2F$), 1.5; 246 ($C_5F_9HN^+$), 39.0; 236 ($M^+ - CF_3H$), 1.1; 196 ($C_4F_7HN^+$), 6.2; 176 ($C_4F_6N^+$), 2.5; 145 ($C_3F_5N^+$), 2.3; 131 ($C_3F_5^+$), 4.5; 119 ($C_2F_5^+$), 2.2; 114 ($C_2F_4N^+$), 1.3; 100 ($C_2F_4^+$), 5.8; 96 ($C_2F_3HN^+$), 4.9; 92 ($C_3F_2H_4N^+$), 9.4; 91 ($C_3F_2H_3N^+$), 13.3; 83 (CF_3N^+), 1.8; 71 ($C_3FH_2N^+$), 22.4; 69 (CF_3^+), 18.5; 60 ($C_2FH_3N^+$), 100. Anal. Calcd for $C_7F_{10}H_4N_2$: C, 27.45; F, 62.1; H, 1.31. Found: C, 27.76; F, 61.9; H, 1.23.

Properties of $CF_2CF_2CF_2CF_2NCHFCF{=}NCH_2CF_3$ (4). Compound **4** is retained as a low volatile colorless liquid in 61% yield in a trap cooled to −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2958 w, vbr, 1779 m, 1765 ms ($\nu_{C=N}$), 1424 ms, 1399 m, 1343 vs, 1275 vs, 1225 vs, 1175 vs, 1145 s, 1103 m, 1078 s, 1034 w, 1002 m, 970 vs, 834 mw, 762 w, 705 vw, 676 vw, 642 w, 574 w, 541 mw, 414 mw. NMR [$CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}NCH^EF^FCF^G{=}NCH_2^HCF_3^I$]: ^{19}F, δ −36.3 (G, br d), −71.9 (I, t), −91.3 (A, AB m), −92.2 (B, AB m), −132.2 (C, AB m), −132.9 (D, AB m), −152.2 (F, dp); ^1H, δ 4.0 (H, quat), 6.05 (E, d). J_{AB} = 176 Hz, J_{CD} = 247 Hz, J_{FG} = 22.9 Hz, J_{EF} = 47.0 Hz, J_{HI} = 8.7 Hz. MS CI [*m/e* (species), intensity]: 375 (MH^+), 0.4; 356 ($MH^+ - F$), 2.0; 355 ($M^+ - F$), 18.8; 335 ($M^+ - HF_2$), 0.4; 305 ($M^+ - CF_3$), 6.5; 246 ($C_5F_9HN^+$), 42.1; 207 ($C_5F_7N^+$), 100; 196 ($C_4F_7HN^+$), 12.0; 176 ($C_4F_6N^+$), 9.1; 145 ($C_3F_5N^+$), 5.9; 133 ($C_3F_5H_2^+$), 5.4; 131 ($C_3F_5^+$), 6.1; 128 ($C_3F_4H_2N^+$), 7.2; 119 ($C_2F_5^+$), 8.0; 114 ($C_2F_4N^+$), 1.0; 107 ($C_3F_3N^+$), 11.6; 100 ($C_2F_4^+$), 5.9; 97 ($C_2F_3H_2N^+$), 6.6; 83 ($C_2F_3H_2^+$), 11.9; 69 (CF_3^+), 36.7.

Properties of $CF_2CF_2OCF_2CF_2NCHFCF{=}NCH_3$ (5). Compound **5** is isolated as a colorless liquid in 74% yield in a trap cooled to −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2990 w, 2954 w, 1774 m/1761 sh ($\nu_{C=N}$), 1415 mw, 1331 sh, 1304 s, 1262, 1225 vs, 1172 ms, 1144 vs, 1086 m, 1059 w, 942 m, 849 m, 800 vw, 736 m, 622 m, 571 w, 550 w, 482 m. NMR [$CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}NCH^EF^FCF^G{=}NCH_3^H$]: ^{19}F, δ −44.2 (G, br d), −86.7 (C, AM m), −87.6 (D, AB m), −93.2 (A, AB m), −95.3 (B, AB m), −155.3 (F, m); ^1H, δ 3.17 (H, s), 6.13 (E, d). J_{AB} = 198 Hz, J_{CD} = 145 Hz, J_{FG} = 23.9 Hz, J_{EF} = 46.1 Hz. MS CI [*m/e* (species), intensity]: 323 (MH^+), 1.8; 321 ($M^+ - H$), 1.1; 303 ($M^+ - F$), 47.1; 284 ($M^+ - 2F$), 1.6; 262 ($C_5F_9HNO^+$), 31.2; 253 ($M^+ - CF_3$), 4.3; 212 ($C_4F_7HNO^+$), 1.2; 192 (C_4F_6NO+), 3.1; 170 ($C_5F_5NH^+$), 5.5; 146 ($C_3F_5HN^+$), 4.8; 145 ($C_3F_5N^+$), 3.6; 131

---

(33) Kotun, S. P.; Anderson, J. D. O.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 1124.

(34) Patel, N. R.; Kirchmeier, R. L. *Inorg. Chem.* **1992**, *31*, 2537.

(35) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 2187.

(36) Lustig, M.; Pitochelli, A. R.; Ruff, J. K.; *J. Am. Chem. Soc.* **1966**, *88*, 4531.

(37) Gould, G. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 3110.

(38) Schack, C. J.; Wilson, R. D.; Warner, M. G. *Inorg. Synth.* **1986**, *24*, 8.

(39) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959.

(40) Silverstein, R. M.; Bassler, G. C. *Spectrometric Identification of Organic Compounds*; John Wiley and Sons Inc.: New York, 1967, 118.

($\mathrm{C_3F_5^+}$), 0.4; 119 ($\mathrm{C_2F_5^+}$), 27.1; 114 ($\mathrm{C_2F_4N^+}$), 6.5; 100 ($\mathrm{C_2F_4^+}$), 12.0; 96 ($\mathrm{C_2F_3HN^+}$), 4.9; 92 ($\mathrm{C_3F_2H_4N^+}$), 15.9; 91 ($\mathrm{C_3F_2H_3N^+}$), 23.5; 72 ($\mathrm{C_3FH_3N^+}$), 1.6; 69 ($\mathrm{CF_3^+}$), 16.9; 60 ($\mathrm{C_2FH_3N^+}$), 100.

Properties of $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CHFCF{=}NCH_2CF_3}$ (6). Compound **6** is a low volatile colorless liquid isolated in 65% yield in a trap cooled to −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2957 w, br, 1780 m ($\nu_{\mathrm{C=N}}$), 1415 w, br, 1351 mw, 1331 mw, 1306 vs, 1260 s, 1227 vs, 1176 vs, 1145 vs. 1086 mw, 972 w, 950 mw, 850 w, 762 w, 623 w, 555 w, 488 vw, 407 w. NMR [$\overline{\mathrm{CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}N}}\mathrm{CH^EF^F\text{-}CF^G{=}NCH_2^HCF_3^I}$]: ^{19}F, δ −37.0 (G, br d), −72.5 (I, t), −87.4 (C, AB m), −87.9 (D, AB m), −93.4 (A, AB m), −95.9 (B, AB m), −156.7 (F, m); ^{1}H, δ 4.0 (H, quat), 6.12 (E, d). J_{AB} = 196 Hz, J_{CD} = 150 Hz, J_{FG} = 24.4 Hz, J_{EF} = 45.8 Hz, J_{HI} = 8.4 Hz. MS CI [*m/e* (species), intensity]: 391 (MH$^+$), 1.2; 372 (MH$^+$ − F), 1.2; 371 (M$^+$ − F), 15.7; 351 (M$^+$ − HF$_2$), 2.3; 321 (M$^+$ − CF$_3$), 2.1; 262 ($\mathrm{C_5F_9HNO^+}$), 100; 224 ($\mathrm{C_5F_7HNO^+}$), 1.2; 212 ($\mathrm{C_4F_7HNO^+}$), 2.3; 192 ($\mathrm{C_4F_6NO^+}$), 4.1; 173 ($\mathrm{C_4F_5NO^+}$), 3.5; 142 ($\mathrm{C_3F_4NO^+}$), 7.1; 133 ($\mathrm{C_3F_5H_2^+}$), 6.1; 131 ($\mathrm{C_3F_5^+}$), 3.9; 128 ($\mathrm{C_3F_4H_2N^+}$), 3.4; 119 ($\mathrm{C_2F_5^+}$), 10.6; 114 ($\mathrm{C_2F_4N^+}$), 2.2; 100 ($\mathrm{C_2F_4^+}$), 4.6; 97 ($\mathrm{C_2F_3H_2N+}$), 4.9; 83 ($\mathrm{C_2F_3H_2^+}$), 24.9; 81 ($\mathrm{C_2F_3^+}$), 24.1; 69 ($\mathrm{CF_3^+}$), 48.0. Anal. Calcd for $\mathrm{C_8F_{13}H_3N_2O}$: F, 63.3. Found: F, 62.8.

Preparation of $\overline{\mathrm{CF_2CF_2CF_2CF_2N}}\mathrm{CHF}\overline{\mathrm{C{=}NCH_2CH_2N}}\mathrm{H}$ (7) and $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CHF}\overline{\mathrm{C{=}NCH_2CH_2N}}\mathrm{H}$ (8). An excess of perfluorovinylamine (**A** or **B**) (~2 mmol) is condensed onto 1 mmol of ethylenediamine at −196 °C. The reaction mixture is then slowly allowed to warm to 25 °C. After the unreacted perfluorovinylamine is removed under vacuum, a white solid is left behind in the reaction flask. About 10 mL of anhydrous diethyl ether is added to the reaction flask and the mixture stirred for ~30 min. Filtration, followed by solvent removal, affords the desired product.

Properties of $\overline{\mathrm{CF_2CF_2CF_2CF_2N}}\mathrm{CHF}\overline{\mathrm{C{=}NCH_2CH_2N}}\mathrm{H}$ (7). Compound **7** is obtained as a white solid in 38% yield based on the quantity of the diamine used. It has a melting point of 98–99 °C. Spectral data obtained are as follows. IR (neat solid/KBr) (cm^{-1}): 3225 mw, br, 2946 w, 2874 w, 1629 vs ($\nu_{\mathrm{C=N}}$), 1504 vs, 1478 s, 1456 m, 1424 ms, 1388 m, 1360 sh, 1327 vs, 1304 ms, 1272 vs, 1247 vs, 1196 vs, 1131 vs, 1115 vs, 1092 s, 1035 vs, 986 vs, 958 vs, 929 m, 898 mw, 765 m, 721 ms, 680 mw, 641 m, 619 mw, 588 mw, 571 mw, 533 ms, 461 mw, 421 w. NMR [$\overline{\mathrm{CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}N}}\mathrm{CH^EF^F}\overline{\mathrm{C{=}NCH_2^GCH_2^HN}}\mathrm{H^I}$]: ^{19}F: δ −89.7 (A, AB m), −93.4 (B, AB m), −130.7 (C, AB m), −134.3 (D, AB m), −150.9 (F, dp); ^{1}H, δ 3.5 (H, br s), 3.9 (G, br s), 5.0 (I, br s), 6.2 (E, d). J_{AB} = 172 Hz, J_{CD} = 247 Hz, $J_{\mathrm{(AB)F}}$ = 10.6 Hz, J_{EF} = 48.8 Hz. MS EI [*m/e* (species), intensity]: 315 (M$^+$), 24.8; 314 (M$^+$ − H), 1.0; 296 (M$^+$ − F), 5.8; 295 (M$^+$− HF), 13.3; 286 (M$^+$ − NCH$_3$), 4.7; 268 (M$^+$ − C$_2$FH$_4$), 14.8; 246 (M$^+$ − C$_3$H$_5$N$_2$), 100; 196 ($\mathrm{C_4F_7HN^+}$), 8.3; 158 ($\mathrm{C_4F_5HN^+}$), 1.2; 146 ($\mathrm{C_3F_5HN^+}$), 2.1; 131 ($\mathrm{C_3F_5^+}$), 3.5; 119 ($\mathrm{C_2F_5^+}$), 3.3; 100 ($\mathrm{C_2F_4^+}$), 7.1; 99 ($\mathrm{C_4FH_4N_2^+}$), 21.8; 96 ($\mathrm{C_2F_3HN^+}$), 10.5; 73 ($\mathrm{C_3FH_4N^+}$), 14.0; 72 ($\mathrm{C_3FH_3N^+}$), 6.8; 69 ($\mathrm{CF_3^+}$), 17.0. Anal. Calcd for $\mathrm{C_8F_9H_6N_3}$: C, 30.48; F, 54.3; H, 1.92. Found: C, 30.33; F, 54.1; H, 1.94.

Properties of $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CHF}\overline{\mathrm{C{=}NCH_2CH_2N}}\mathrm{H}$ (8). Compound **8** is obtained as a white solid in 37% yield based on quantity of the diamine used. It has a melting point of 58–59 °C. Spectral data are as follows: IR (neat solid/KBr) (cm^{-1}): 3220 w, br, 2979 w, 2887 w, 1765 mw, 1627 vs ($\nu_{\mathrm{C=N}}$), 1479 m, 1471 m, 1461 m, 1370 m, 1299 vs, 1278 sh, 1208 vs, 1159 sh, 1131 vs, 1111 vs, 1081 s, 1055 ms, 974 m, 939 ms, 918 m, 882 vw, 833 mw, 725 w, 700 w, 677 vw, 633 vw, 620 m. NMR [$\overline{\mathrm{CF_2^ACF_2^{BC}OCF_2^{BC}CF_2^AN}}\mathrm{CH^DF^E}\overline{\mathrm{C{=}NCH_2^FCH_2^FN}}\mathrm{H^G}$]: ^{19}F, δ −86.3 (B, AB m), −88.4 (C, AB m), −94.0 (A, br s), −155.7 (E, dp); ^{1}H, δ 3.6 (F, br s), 6.2 (G, br s), 6.3 (D, d). J_{BC} = 145 Hz, J_{DE} = 46 Hz, J_{AE} = ~9.3 Hz; MS EI [*m/e* (species), intensity]: 331 (M$^+$), 25.9; 330 (M$^+$ − H), 1.6; 312 (M$^+$ − F), 7.1; 311 (M$^+$ − HF), 9.6; 302 (M$^+$ − C$_2$H$_5$), 6.7; 292 (M$^+$ − HF$_2$), 4.4; 290 (M$^+$ − C$_2$H$_3$N), 4.8; 284 (M$^+$ − C$_2$H$_4$F), 30.9; 262 ($\mathrm{C_5F_9HNO^+}$), 84.1; 245 ($\mathrm{C_5F_9N^+}$), 0.5; 212 (M$^+$ − C$_2$F$_5$), 0.5; 192 ($\mathrm{C_4F_6NO^+}$), 1.2; 164 ($\mathrm{C_3F_6N^+}$), 3.1; 146 ($\mathrm{C_3F_5HN^+}$), 14.6; 145 ($\mathrm{C_3F_5N^+}$), 8.8; 135 ($\mathrm{C_2F_5O^+}$), 5.5; 119 ($\mathrm{C_2F_5^+}$), 66.7; 114 ($\mathrm{C_2F_4N^+}$), 19.2; 100 ($\mathrm{C_2F_4^+}$), 34.9; 99 ($\mathrm{C_4FH_4N_2^+}$), 58.9; 96 ($\mathrm{C_2F_3HN^+}$), 100; 73 ($\mathrm{C_3FH_4N^+}$), 63.8; 72 ($\mathrm{C_3FH_3N^+}$), 18.4; 69 ($\mathrm{C_3H_5N_2^+}$), 47.2.

Preparation of $\overline{\mathrm{CF_2CF_2CF_2CF_2N}}\mathrm{CF{=}CFR}$ and $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CF{=}CFR}$ (R = $\mathrm{CH_3}$, $\mathrm{C_4H_9}$). A reaction tube fitted with a Kontes Teflon stopcock and a B-10 joint side arm fitted with a rubber septum is evacuated. A volume of solution containing 1.6 mmol of methyl/*n*-butyllithium in a solvent (diethyl ether or hexane) is syringed into the tube via the septum. The solution is pumped at −196 °C for about 30 min followed by transfer of the perfluorovinylamine (**A** or **B**) (1.6 mmol) under vacuum. The reaction mixture is then allowed to warm slowly to 25 °C and stirred for ~16 h. The products are isolated by trap-to-trap distillation.

Properties of $\overline{\mathrm{CF_2CF_2CF_2CF_2N}}\mathrm{CF{=}CFCH_3}$ (9). Compound **9** is found as a colorless liquid in 76% yield in a trap cooled to −30 °C having passed −10 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 2997 w, 2944 w, 1758 w ($\nu_{\mathrm{C=C}}$), 1441 w, 1409 m, 1397 ms, 1348 vs, 1281 vs, 1222 vs, 1203 sh, 1167 s, 1135 s, 1032 s, 971 vs, 879 mw, 821 sh, 802 m, 736 m, 684 vw, 639 w, 601 mw, 555 m, 497 m, 482 sh, 438 w, 416 w. NMR [$\overline{\mathrm{CF_2^ACF_2^BCF_2^BCF_2^AN}}\mathrm{CF^C{=}CF^DCH_3^E}$]: ^{19}F, δ −92.4 (A, s), −129.5 (C, AB qp, 8 line), −132.4 (B, s), −134.5 (D, AB qp, 14 lines); ^{1}H, δ 2.17 (E, dd). J_{CD} = 129 Hz, J_{CE} = 5.3 Hz, J_{DE} = 16.87 Hz. MS CI [*m/e* (species), intensity]: 292 (MH$^+$), 6.1; 291 (M$^+$), 85.6; 273 (MH$^+$ − F), 6.7; 272 (M$^+$ − F), 100; 222 (M$^+$ − CF$_3$), 3.1; 196 ($\mathrm{C_4F_7HN^+}$), 0.5; 191 ($\mathrm{C_5F_6H_3N^+}$), 5.0; 176 ($\mathrm{C_4F_6N^+}$), 1.7; 172 ($\mathrm{C_5F_5H_3N^+}$), 5.2; 145 ($\mathrm{C_3F_5N^+}$), 3.1; 141 ($\mathrm{C_4F_4H_3N^+}$), 6.6; 140 ($\mathrm{C_4F_4H_2N^+}$), 6.4; 131 ($\mathrm{C_3F_5^+}$), 9.7; 122 ($\mathrm{C_4F_3H_3N^+}$), 15.7; 119 ($\mathrm{C_2F_5^+}$), 3.6; 114 ($\mathrm{C_2F_4N^+}$), 4.1; 100 ($\mathrm{C_2F_4^+}$), 16.4; 95 ($\mathrm{C_2F_3N^+}$), 9.2; 77 ($\mathrm{CF{=}CFCH_3^+}$), 26.6; 69 ($\mathrm{CF_3^+}$), 43.8; 65 ($\mathrm{C_2F_2H_3^+}$), 30.4. Anal. Calcd for $\mathrm{C_7F_{10}H_3N}$: C, 28.89; H, 1.04. Found: C, 29.13; H, 1.09.

Properties of $\overline{\mathrm{CF_2CF_2CF_2CF_2N}}\mathrm{CF{=}CFC_4H_9}$ (10). This compound is isolated as a colorless liquid in 67% yield in a trap at −20 °C. Spectral data are as follows. IR (gas) (cm^{-1}): 2973 m, 2945 m, 2880 w, 1776 w, br ($\nu_{\mathrm{C=C}}$), 1411 m, 1349 s, 1306 m, 1280 vs, 1225 vs, 1175 vs, 1142 ms, 1078 mw, 1023 mw, 1001 w, 971 vs, 879 vw, 835 w, 744 w, 641 w, 604 w, 557 w. NMR [$\overline{\mathrm{CF_2^ACF_2^BCF_2^BCF_2^AN}}\mathrm{CF^C{=}CF^DCH_2^ECH_2^F\text{-}CH_2^GCH_3^H}$]: ^{19}F, δ −92.4 (A, s), −132.6 (B, s), −135.1 (C, AB tp – 7 lines), −136.6 (D, AB tp – 13 lines); ^{1}H, δ 0.94 (H, t), 1.4 (G, m), 1.6 (F, m), 2.5 (E, tdd – 12 lines). J_{CD} = 134 Hz, J_{CE} = ~5.3 Hz, J_{DE} = 21.8 Hz, J_{AC} = J_{AD} = 5.6 Hz, J_{EF} = J_{FG} = J_{GH} = ~7.3 Hz. MS CI [*m/e* (species), intensity]: 334 (MH$^+$), 1.9; 333 (M$^+$), 19.2; 315 (MH$^+$ − F), 11.0; 314 (M$^+$ − F), 100; 290 (M$^+$ − C$_3$H$_7$), 44.7; 272 (M$^+$ − C$_3$FH$_6$), 46.2; 259 (M$^+$ − C$_4$FH$_7$), 4.3; 254 (M$^+$ − C$_3$F$_2$H$_5$), 5.6; 241 (M$^+$ − C$_4$F$_2$H$_6$), 9.3; 214 ($\mathrm{C_4F_8N^+}$), 0.5; 171 ($\mathrm{C_6F_4H_9N^+}$), 2.5; 145 ($\mathrm{C_3F_5N^+}$), 2.5; 131 ($\mathrm{C_3F_5^+}$), 5.3; 119 ($\mathrm{C_2F_5^+}$ or $\mathrm{C_6F_2H_9^+}$), 5.6; 114 ($\mathrm{C_2F_4N^+}$), 2.5; 100 ($\mathrm{C_2F_4^+}$), 8.7; 99 ($\mathrm{C_6FH_8^+}$), 18.2; 69 ($\mathrm{CF_3^+}$), 35.8. Anal. Calcd. for $\mathrm{C_{10}F_{10}H_9N}$: C, 36.04; F, 57.0; H, 2.70. Found: C, 36.25; F, 56.9; H, 2.61.

Properties of $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CF{=}CFCH_3}$ (11). Compound **11** is isolated as a colorless liquid in 82% yield in a trap at −30 °C. Spectral data are as follows. IR (gas) (cm^{-1}): 2980 w, 2943 w, 1765 w ($\nu_{\mathrm{C=C}}$), 1444 w, 1415 w, 1397 mw, 1345 sh, 1321 vs, 1281 s, 1258 s, 1225 vs, 1191 s, 1144 vs, 1090 s, 975 m, 933 s, 806 m, 736 m, 680 mw, 626 w, 511 mw, 482 mw. NMR [$\overline{\mathrm{CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}N}}\mathrm{CF^E{=}CF^FCH_3^G}$]: ^{19}F, δ −85.7 (C, AB m), −89.4 (D, AB m), −90.8 (A, AB m), −129.3 (E, AB qp, 8 line), −134.3 (F, AB qp, 14 lines); ^{1}H, δ 2.15 (G, dd). J_{AB} = 187 Hz, J_{CD} = 134 Hz, J_{EF} = 127 Hz J_{EG} = 5.3 Hz, $J_{\mathrm{(AB)E}}$ = $J_{\mathrm{(AB)F}}$ = 5.6 Hz, J_{FG} = 16.8 Hz; MS CI [*m/e* (species), intensity]: 308 (MH$^+$), 6.7; 307 (M$^+$), 66.0; 289 (MH$^+$ − F), 8.3; 288 (M$^+$ − F), 100; 238 (M$^+$ − CF$_3$), 5.7; 191 ($\mathrm{C_5F_6H_3N^+}$), 5.2; 172 ($\mathrm{C_5F_5H_3N^+}$) 5.0; 145 ($\mathrm{C_3F_5N^+}$), 1.0; 141 ($\mathrm{C_4F_4H_3N^+}$), 36.2; 140 ($\mathrm{C_4F_4H_2N^+}$), 12.3; 122 ($\mathrm{C_4F_3H_3N^+}$), 11.3; 119 ($\mathrm{C_2F_5^+}$), 22.0; 114 ($\mathrm{C_2F_4N^+}$), 5.4; 100 ($\mathrm{C_2F_4^+}$), 24.0; 95 ($\mathrm{C_2F_3N^+}$), 8.3; 77 ($\mathrm{C_3F_2H_3^+}$), 20.8; 69 ($\mathrm{CF_3^+}$), 35.9; 65 ($\mathrm{C_2F_2H_3^+}$), 21.0. Anal. Calcd for $\mathrm{C_7F_{10}H_3NO}$: C, 27.36; F, 61.9; H, 0.98. Found: C, 27.25; F, 61.5; H, 0.95.

Properties of $\overline{\mathrm{CF_2CF_2OCF_2CF_2N}}\mathrm{CF{=}CFC_4H_9}$ (12). This compound is isolated as a colorless liquid in 68% yield in a trap cooled to −20 °C having passed a trap at −5 °C. Spectral data are as follows. IR (gas) (cm^{-1}): 2972 w, 2944 w, 2880 mw, 1780, 1765 w ($\nu_{\mathrm{C=C}}$), 1414 mw, 1346 ms, 1321 s, 1276 s, 1224 vs, 1176 s, 1143 s, 1104 m, 1082 mw, 1041 w, 971 ms, 932 ms, 853 w, 792 vw, 737 w, 640 vw, 482 vw, 427 vw. NMR [$\overline{\mathrm{CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}N}}\mathrm{CF^E{=}CF^FCH_2^GCH_2^HCH_2^ICH_3^J}$]: ^{19}F, δ −85.8 (C, AB m), −89.6 (D, AB m), −90.8 (A, AB m), −99.5 (B, AB m), −129.5 (E, AB tp, 7 lines), −136.3 (F, AB tp, 13 lines); ^{1}H, δ 0.94 (J, t), 1.39 (I, m), 1.6 (H, m), 2.49 (G, tdd, 12 lines). J_{AB} = 190 Hz, J_{CD} = 145 Hz, J_{EF} = 127 Hz, J_{EG} = ~5.3 Hz, J_{FG} = 21.7 Hz, J_{AC} = $J_{\mathrm{(AB)E}}$ = $J_{\mathrm{(AB)F}}$ = ~5.6 Hz, J_{GH} = J_{HI} = J_{IJ} = ~7.3 Hz. MS CI [*m/e* (species), intensity]: 350 (MH$^+$), 4.7; 349 (M$^+$), 32.0; 331 (MH$^+$ − F), 19.0; 330 (M$^+$ − F), 100; 306 (M$^+$ − C$_3$H$_7$), 19.1; 289 (M$^+$ − C$_3$FH$_5$), 5.9; 288 (M$^+$

$- C_3FH_6$), 74.9; 270 ($M^+ - C_3F_2H_5$), 7.2; 257 ($M^+ - C_4F_2H_6$), 16.6; 244 ($M^+ - C_5F_2H_7$), 6.6; 214 ($C_4F_8N^+$), 1.2; 190 ($C_6F_5H_9N^+$), 5.1; 172 ($C_6F_4H_8O^+$), 5.9; 140 ($C_4F_4O^+$), 14.0; 119 ($C_2F_5^+$ or $C_6F_2H_9^+$), 32.5; 100 ($C_2F_4^+$), 11.7; 99 ($C_6FH_8^+$), 30.5; 69 (CF_3^+), 32.4. Anal. Calcd for $C_{10}F_{10}H_9NO$: C, 34.38; F, 54.4; H, 2.58. Found: C, 34.55; F, 54.4; H, 2.48.

Preparation of $CF_2CF_2CF_2CF_2NCF{=}CFN(CH_3)_2$ (13) and $CF_2CF_2OCF_2CF_2NCF{=}CFN(CH_3)_2$ (14). A slight excess of perfluorovinylamine (**A** or **B**) (~1.1 mmol) is condensed onto 1 mmol of (dimethylamino)trimethylsilane at −196 °C. The reaction mixture is then warmed slowly to 25 °C. The product is obtained following trap-to-trap distillation of the reaction mixture.

Preparation of $CF_2CF_2CF_2CF_2NCF{=}CFN(CH_3)_2$ (13). This compound is isolated as a colorless moisture sensitive liquid in 62% yield in a trap cooled to −10 °C. Spectral data are as follows. IR (gas in equilibrium with liquid) (cm^{-1}): 2935 m, 2827 m, br, 1743 vs ($\nu_{C=C}$), 1498 m, 1459 ms, 1411 s, 1385 s, 1341 s, 1271 s, 1212 vs, 1178 s, 1157 s, 1126 s, 1089 s, 1027 ms, 1008 ms, 963 s, 932 ms, 889 w, 871 m, 787 mw, 763 m, 744 mw. NMR [$CF_2^ACH_2^BCF_2^BCF_2^ANCF^C{=}CF^DN(CH_3)_2^E$] ^{19}F, δ −93.7 (A, br s), −120.2 (C, br d), −133.3 B, br s), −156.3 (D, br d); ^1H, δ 2.8 (E, br s). J_{CD} = 110 Hz. MS CI [*m/e* (species), intensity]: 321 (MH^+), 15.2; 320 (M^+), 42.0; 302 ($MH^+ - F$), 10.5; 301 ($M^+ - F$), 82.3; 299 ($M^+ - H_2F$), 59.4; 274 ($M^+ - C_2FH_3$), 23.0; 271 ($M^+ - C_2FH_6$), 36.1; 246 ($C_5F_9HN^+$), 22.1; 229 ($C_5F_8H_3N^+$), 3.5; 196 ($C_4F_7HN^+$), 12.8; 176 ($C_4F_6N^+$), 7.8; 170 ($C_5F_4H_6N_2^+$), 11.7; 155 ($C_4F_4H_3N_2^+$), 22.1; 151 ($C_3F_6H^+$), 14.0; 131 ($C_3F_5^+$), 4.7; 119 ($C_2F_5^+$), 9.4; 114 ($C_2F_4N^+$), 2.2; 109 ($C_3F_3H_2N^+$), 16.3; 107 ($C_4F_2H_7N^+$), 10.9; 106 ($C_4F_2H_6N^+$), 7.0; 100 ($C_2F_4^+$), 1.2; 94 ($C_3F_2H_6N^+$), 24.6; 79 ($C_2F_2H_3N^+$), 32.6; 70 $C_3H_6N_2^+$), 100; 69 (CF_3^+), 26.6.

Properties of $CF_2CF_2OCF_2CF_2NCF{=}CFN(CH_3)_2$ (14). This compound is isolated as a colorless moisture sensitive liquid in 67% yield in a trap cooled to −10 °C. Spectral data are as follows. IR (gas in equilibrium with liquid) (cm^{-1}): 2934 m, 2827 mw, br, 1747 s ($\nu_{C=C}$), 1499 ms, 1459 m, 1414 sh, 1390 s, 1312 vs, 1249 vs, 1208 vs, 1172 vs, 1132 vs, 1084 vs, 1022 w, 970 w, 924 vs, 824 w, 787 mw, 767 ms, 723 w. NMR [$CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}NCF^E{=}CF^FN(CH_3)_2^G$]: ^{19}F, δ −85.5 (C, AB m), −88.9 (D, AB m), −90.9 (A, AB m), −99.0 (B, AB m), −119.1 (E, AB m), −154.4 (F, AB m); ^1H, δ 2.84 (G, br s). J_{AB} = 194 Hz, J_{CD} = 149 Hz, J_{EF} = 109 Hz. MS CI [*m/e* (species), intensity]: 337 (MH^+), 17.8; 336 (M^+), 59.1; 318 ($MH^+ - F$), 7.2; 317 ($M^+ - F$), 100; 315 ($M^+ - H_2F$), 7.1; 287 ($M^+ - C_2FH_6$), 4.4; 262 ($C_5F_9HNO^+$), 0.5; 237 ($M^+ - C_3F_3H_6$), 2.5; 217 ($M^+ - C_2F_5$), 2.5; 192 ($C_4F_6NO^+$), 1; 170 ($C_5F_4H_6N_2^+$), 13.0; 155 ($C_4F_4H_3N_2^+$), 22.1; 147 ($C_3F_5O^+$), 1.0; 131 ($C_3F_5^+$), 0.5; 119 ($C_2F_5^+$), 10.9; 114 ($C_2F_4N^+$), 5.5; 109 ($C_3F_3H_2N^+$), 16.3; 106 ($C_4F_2H_6N^+$), 9.9; 100 ($C_2F_4^+$), 5.4; 94 ($C_3F_2H_6N^+$), 12.8; 79 ($C_2F_2H_3N^+$), 5.8; 70 $C_3H_6N_2^+$), 5.9; 69 (CF_3^+), 8.9.

Reaction with Electrophiles. Reaction of Perfluorovinylamines with Chlorine(I) Fluoride. The reagents, ClF (~6 mmol) and perfluorovinylamine (**A**, **B**, **C**, or **D**) (~5 mmol) are condensed into a 30-mL stainless steel Hoke cylinder at −196 °C and allowed to warm slowly to 25 °C. The products are then separated by trap-to-trap distillation. Volatile materials retained in traps at −78 and −110 °C traps are combined and purified by gas chromatography by using a Kel-F No. 90 column (4 m) at 100 °C.

Properties of $(CF_3)_2NCFClCF_3$ (15) and $(CF_3)_2NCF_2CF_2Cl$ (16). A mixture containing 31 parts of $(CF_3)_2NCFClCF_3$ and 69 parts of $(CF_3)_2NCF_2CF_2Cl$ is obtained in 95.4% yield. The isomers are not separated by GC. Spectral data obtained for the mixture of [$(CF_3^A)_2NCF^BClCF_3^C$] and [$(CF_3^D)_2NCF_2^ECF_2^FCl$] are as follows. IR (gas) (cm^{-1}): 1353 vs, 1292 m, 1260 s, 1228 vs, 1196 m, 1171 m, 1147 w, 1122 m, 999 s, 940 w, 888 w, 863 m, 847 s, 771 m, 738 m, 700 vw, 660 vw, 558 vw. NMR: ^{19}F, δ −52.2 (D, dq), −52.9 (A, tt), −71.3 (C, sept), −82.2 (F, m), −93.3 (B, sept), −106.2 (E, m). J_{AB} = 16.1 Hz, J_{AC} = 7.5 Hz, J_{DE} = 11.8 Hz, J_{DF} = 6.2 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 252 ($M^+ - Cl$), 1.8; 202 ($M^+ - CF_2Cl$), 16.1; 164 ($C_3F_6N^+$), 17.9; 135 ($C_2F_4Cl^+$), 28.6; 119 ($C_2F_5^+$), 5.4; 114 ($C_2F_4N^+$), 37.5; 85 (CF_2Cl^+), 14.3; 69 (CF_3^+), 100.

Properties of $CF_2CF_2CF_2CF_2NCF_2CF_2Cl$ (17), $CF_2CF_2CF_2CF_2NCFClCF_3$ (18), and $CF_2CF_2CF_2CF_2NCFClCF_2Cl$ (19). A mixture containing 33 parts of **17** and 67 parts of **18** is obtained in 61.2% yield. Also obtained is **19** in 16.5% yield which was separated by preparative gas chromatography of this mixture by using a Kel-F No. 90 column (4 m) at 100 °C. Isomers **17** and **18** could not be separated by gas chromatography. Spectral data obtained for the mixture of **17** and **18** are as follows. IR (gas) (cm^{-1}): 1403 w, 1343 s, 1282 m, 1240 vs, 1179 m, 1127 m, 1078 m, 1037 w, 1019 w, 980 s, 947 m, 869 w, 804 w, 781 m, 722 w, 675 w, 620 w, 562 w. NMR [$CF_2^ACF_2^BCF_2^BCF_2^ANCF_2^CCF_2^DCl$] and [$CF_2^ECF_2^FCF_2^FCF_2^ENCF^GClCF_3^H$]: ^{19}F, δ −72.1 (D, pt), −82.9 (H, dp), −90.9 (B, F, m), −94.2 (C, p), −106.5 (G, pq), −133.0 (E, m), −133.3 (A, m). J_{BC} = 12.4 Hz, J_{BD} = 10.4 Hz, J_{CD} = 2.0 Hz, J_{FG} = 14.5 Hz, J_{FH} = 8.3 Hz, J_{GH} = 6.2 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 330 ($M^+ - F$), 11.9; 314 ($M^+ - Cl$), 63.4; 280 ($M^+ - CF_3$), 68.3; 264 ($M^+ - CF_2Cl$), 89.1; 230 ($C_4F_7NCl^+$), 13.9; 214 ($C_4F_8N^+$), 19.8; 176 ($C_4F_6N^+$), 14.9; 164 ($C_3F_6N^+$), 20.8; 135 ($C_2F_4Cl^+$), 100; 119 ($C_2F_5^+$), 39.6; 114 ($C_2F_4N^+$), 32.7; 100 ($C_2F_4^+$), 39.6; 85 (CF_2Cl^+), 30.7; 69 (CF_3), 69.3. Spectral data obtained for **19** are as follows. IR (gas) (cm^{-1}): 1344 s sh, 1331 vs, 1287 s, 1249 s, 1216 s, 1195 s, 1165 vs. 1132 m, 1119 s, 1086 m, 1038 s, 969 vs, 868 w, 817 s, 759 m, 721 m, 672 w, 644 w, 623 w, 612 w, 575 w, 558 m. NMR [$CF_2^ACF_2^BCF_2^BCF_2^ANCF^CClCF_2^DCl$]: ^{19}F, δ −67.5 (D, m), −89.6 (B, m), −101.8 (C, pt), −133.2 (A, m). J_{AB} = 178 Hz, J_{BD} = 12.4 Hz, J_{BC} = 14.9 Hz, J_{CD} = 7.5 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 330 ($M^+ - Cl$), 34.1; 280 ($M^+ - CF_2Cl$), 94.5; 230 ($C_4F_7NCl^+$), 19.7; 151 ($C_2F_3Cl_2^+$), 47.0; 135 ($C_2F_4Cl^+$), 53.3; 131 ($C_3F_5^+$), 18.3, 100 ($C_2F_4^+$), 36.3; 85 (CF_2Cl^+), 40.1; 69 (CF_3^+), 100.

Properties of $CF_2CF_2OCF_2CF_2NCF_2CF_2Cl$ (20) and $CF_2CF_2OCF_2CF_2NCFClCF_3$ (21). A mixture containing 84 parts of **20** and 16 parts of **21** is obtained in 87% yield. Spectral data obtained for the mixture are as follows. IR (gas) (cm^{-1}): 1370 m, 1310 s, 1300 sh, 1230 vs, 1192 s, 1181 s, 1150 s, 1130 w, 1114 w, 1000 m, 972 m, 961 m, 932 m, 801 w, 780 m, 672 w, 637 w, 630 w, 490 w. NMR [$CF_2^ACF_2^BOCF_2^BCF_2^ANCF_2^CCF_2^DCl$] and [$CF_2^ECF_2^FOCF_2^FCF_2^ENCF^GClCF_3^H$]: ^{19}F, δ −72.0 (D, m), −83.5 (H, m), −86.0 (E, s), −87.0 (A, s), −92.0 (F, m), −92.5 (B, C, m), −104.0 (G, m). MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 330 ($M^+ - Cl$), 3.9; 296 ($M^+ - CF_3$), 35.3; 280 ($M^+ - CF_2Cl$), 35.3; 192 ($C_4F_6NO^+$), 9.8; 180 ($C_3F_5NCl^+$), 4.9; 164 ($C_3F_6N^+$), 21.6; 135 ($C_2F_4Cl^+$), 51.0; 119 ($C_2F_5^+$), 100; 114 ($C_2F_4N^+$), 54.9; 100 ($C_2F_4^+$), (52.9; 85 (CF_2Cl^+), 19.6; 69 (CF_3^+), 35.3. Anal. Calcd for $C_6F_{12}ClNO$: C, 19.70; F, 62.4. Found: C, 19.59; F, 62.0.

Properties of $CF_2CF_2CF_2CF_2CF_2NCF_2CF_2Cl$ (22) and $CF_2CF_2CF_2CF_2CF_2NCFClCF_3$ (23). A mixture containing 93 parts of **22** and 7 parts of **23** is obtained in 80% yield. Spectral data obtained for the mixture are as follows. IR (gas) (cm^{-1}): 1372 m, 1347 sh, 1329 vs, 1296 sh, 1275 s, 1235 s, 1213 vs, 1193 vs, 1172 s, 1133 s, 1107 m, 1070 m, 1060 sh, 1027 s, 977 s, 957 m, 909 w, 852 w, 823 vw, 810 w, 797 m, 773 s, 657 m, 637 m, 588 w, 519 w, 482 w. NMR [$CF_2^ACF_2^BCF_2^CCF_2^BCF_2^ANCF_2^DCF_2^ECl$] and [$CF_2^FCF_2^GCF_2^HCF_2^GCF_2^FNCF^IClCF_3^J$]: ^{19}F, δ −72.7 (E, m), −84.4 (J, m), −91.5 (H, m), −91.7 (C, D, m), −106.7 (I, m), −131.5 (G, m), −132.5 (B, m), −133.0 (F, m), −134.7 (A, m). MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 380 ($M^+ - F$), 4.5; 364 ($M^+ - Cl$), 10.6; 314 ($M^+ - CF_2Cl$), 77.3; 264 ($C_5F_{10}N^+$), 10.6; 226 ($C_5F_8N^+$), 19.7; 214 ($C_4F_8N^+$), 4.5; 176 ($C_4F_6N^+$), 6.1; 164 ($C_3F_6N^+$), 9.1; 135 ($C_2F_4Cl^+$), 100; 131 ($C_3F_5^+$), 22.7; 119 ($C_2F_5^+$), 69.7; 114 ($C_2F_4N^+$), 31.8; 100 ($C_2F_4^+$), 51.5; 85 (CF_2Cl^+), 34.8; 69 (CF_3^+), 86.4. Anal. Calcd for $C_7F_{14}ClN$: C, 21.03; F, 66.6. Found: C. 21.22; F, 66.1.

Reaction of Perfluorovinylamines with Chlorine Fluorosulfate. In a 30-mL stainless steel Hoke cylinder, excess chlorine fluorosulfate (6 mmol) is added to the perfluorovinylamine (**A**, **C**, or **D**) (5 mmol) at 196 °C. The reaction mixture is allowed to warm slowly to 25 °C over a period of ~24 h. The cylinder is then cooled to −78 °C, and all volatile materials are pumped off from the reaction mixture. The residual volatile liquid is transferred onto mercury and agitated until it becomes colorless. This liquid is then purified by preparative gas chromatography by using a Kel-F No. 90 column (4 m) at 100 °C.

Properties of $(CF_3)_2NCF(OSO_2F)CF_2Cl$ (24) and $(CF_3)_2NCFClCF_2(OSO_2F)$ (25). A mixture containing 82 parts of **24** and 18 parts of **25** is obtained in 65% yield. Spectral data obtained for the mixture of **24** and **25** are as follows. IR (gas) (cm^{-1}): 1497 s, 1360 vs, 1324 s, 1270 sh, 1257 s, 1230 vs, 1184 w, 1170 w, 1160 w, 1130 w, 1090 m, 1030 w, 995 s, 980 m, 960 sh, 890 w, 852 s, 762 w, 752 vw, 734 w, 690 vw, 580 m, 570 sh. NMR: $[(CF_3{}^A)_2NCF^B(OSO_2F^C)CF_2{}^DCl]$ and $[(CF_3{}^E)_2NCF^FClCF_2{}^G(OSO_2F^H)]$ ^{19}F, δ +51.3 (C, d), +49.7 (H, t), −51.9 (A, E, dt), −69.7 (D, sept), − 83.0 (G, m), −105.0 (F, m), −105.3 (B, dsept). J_{AB} = 16.1 Hz, J_{AC} = 7.5 Hz, J_{BC} = 13.6 Hz, J_{GH} = 8.5 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 332 (M^+ − Cl), 1.0; 282 (M^+ − CF_2Cl), 15.8; 268 (M^+ − OSO_2F), 6.9; 215 ($CFClCF_2SO_3F^+$), 5.9; 199 ($C_2F_4SO_3F^+$), 5.0; 180 ($C_3F_5NCl^+$), 16.8; 164 ($C_3F_6N^+$), 11.9; 113 (CF_2COCl^+), 8.9; 114 ($C_2F_4N^+$), 17.8; 97 (CF_2COF^+), 13.9; 85 (CF_2Cl^+), 17.8; 83 (SO_2F^+), 25.7; 69 ($CF_3{}^+$), 100. Anal. Calcd for $C_4F_{10}ClNO_3S$: C, 13.06; F, 51.7. Found: C, 13.29; F, 51.4.

Properties of $CF_2CF_2CF_2CF_2NCF(OSO_2F)CF_2Cl$ (26) and $CF_2CF_2CF_2CF_2NCFClCF_2(OSO_2F)$. (27). A mixture containing 50 parts of **26** and 50 parts of **27** is obtained in 76% yield. Spectral data obtained for the mixture are as follows. IR (gas) (cm^{-1}): 1500 s, 1347 s, 1305 sh, 1277 s, 1259 s, 1231 vs, 1199 m, 1185 m, 1132 m, 1079 m, 1035 w, 1002 vw, 984 s, 980 sh, 975 sh, 875 sh, 849 s, 791 w, 745 vw, 673 vw, 622 vw, 580 m, 565 m. NMR $[CF_2{}^ACF_2{}^BCF_2{}^BCF_2{}^ANCF^C(OSO_2F^D)CF_2{}^ECl]$ and $[CF_2{}^FCF_2{}^GCF_2{}^GCF_2{}^FNCF^HClCF_2{}^IOSO_2F^J]$: ^{19}F, δ +51.6 (D, d), +49.8 (J, t), −70.7 (E, dp), ∼−90 (B, G, AB m), −106.2 (H, pt), −108.6 (C, dp), ∼−133 (A, F, AB m). J_{BC} = 14.3 Hz, J_{BE} = 7.5 Hz, J_{CD} = 12.4 Hz, J_{CE} = 2.5 Hz, J_{GH} = 21.1 Hz, J_{HI} = 6.2 Hz, J_{IJ} = 8.1 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 394 (M^+ − Cl), 20.0; 344 (M^+ − CF_2Cl), 28.3; 330 (M^+ − OSO_2F), 30.0; 280 (M^+ − $CF_2SO_3F^+$), 51.7; 242 ($C_5F_8NO^+$), 30.0; 215 ($CF_2ClCFSO_3F^+$), 13.3; 200 ($C_4F_8{}^+$), 5.0; 175 ($CF_2NCOSO_2F^+$), 15.0; 135 ($C_2F_4Cl^+$), 41.7; 100 ($C_2F_4{}^+$), 33.0; 85 (CF_2Cl^+), 4.7; 83 (SO_2F^+), 100; 69 ($CF_3{}^+$), 80.0.

Properties of $CF_2CF_2CF_2CF_2CF_2NCF(OSO_2F)CF_2Cl$ (28). Compound **28** is obtained as the only addition isomer in 80% yield. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1499 s, 1370 m, 1340 m, 1313 s, 1280 vs, 1263 vs, 1238 vs, 1200 sh, 1132 m, 1075 s, 1025 s, 1003 w, 977 s, 955 sh, 850 s, 790 w, 785 w, 713 w, 675 w, 650 w, 582 w. NMR $[CF_2{}^ACF_2{}^BCF_2{}^CCF_2{}^BCF_2{}^ANCF^D(OSO_2F^E)CF_2{}^FCl]$: ^{19}F, δ 52.3 (E, d), −71.5 (F, p), −90.1 (C, AB m), −131.8 (B, AB m), −134.4 (A, AB m). J_{CF} = 12.4 Hz, J_{DE} = 9.9 Hz. MS EI [*m/e* (species), intensity] (correct isotopic ratio is observed): 444 (M^+ − Cl), 13.3; 394 (M^+ − CF_2Cl), 43.3; 380 (M^+ − OSO_2F), 33.3; 330 (M^+ − $CF_2SO_3F^+$), 13.3; 292 ($C_6F_{10}NO^+$), 30.0; 226 ($C_5F_8N^+$), 18.3; 215 ($CFClCF_2SO_3F^+$), 30.0; 199 ($C_2F_4SO_3F^+$), 13.3; 135 ($C_2F_4Cl^+$), 33.3; 131 ($C_3F_5{}^+$), 23.3; 119 ($C_2F_5{}^+$), 26.7; 114 ($C_2F_4N^+$), 11.7; 113 (CF_2COCl^+), 26.7; 100 ($C_2F_4{}^+$), 26.7; 97 (CF_2COF^+), 41.7; 85 (CF_2Cl^+), 51.7; 83 (SO_2F^+), 100; 69 ($CF_3{}^+$), 76.7. Anal. Calcd for $C_7F_{14}ClNO_3S$: C, 17.52; F, 55.5. Found: C, 17.93; F, 55.8.

Reaction of Perfluorovinylamines with Hypohalites. (a) Pentafluorosulfur(VI) Hypochlorite. The perfluorovinylamine (A or B) (1 mmol) and pentafluorosulfur(VI) hypohalite (1.2 mmol) are condensed into a reactor at −196 °C fitted with a Kontes Teflon stopcock and allowed to warm slowly to 25 °C. The products are then separated by trap-to-trap distillation.

Properties of $CF_2CF_2CF_2CF_2NCF(OSF_5CF_2Cl)$ (29) and $CF_2CF_2CF_2CF_2NCFClCF_2(OSF_5$ (30). A mixture of isomers containing 38 parts of **29** and 62 parts of **30** is obtained in 57% yield in a trap at −10 °C. Spectral data obtained for this mixture are as follows. IR (gas) (cm^{-1}): 1401 w, 1341 vs, 1303 ms, 1270 s, 1229 vs, 1191 vs, 1131 s, 1080 m, 1038 m, 979 vs, 944 vs, 929 vs, 881 s, 820 s, 778 m, 754 m, 737 m, 713 w, 676 w, 653 vw, 619 vw, 603 s, 561 mw, 481 w, 433 vw, 413 w. NMR: $[CF_2{}^{AB}CF_2{}^{CD}CF_2{}^{CD}CF_2{}^{AB}NCF^E(OSF_4{}^FF^G)CF_2{}^{HI}Cl]$ and $[CF_2{}^{JK}CF_2{}^LCF_2{}^LCF_2{}^{JK}NCF^MClCF_2{}^{NO}OSF_4{}^PF^Q]$: ^{19}F, δ 73.0 (P, dm), 71.9 (F, brt), 61.4 (G, m), 60.5 (Q, m), −70.1 (H, AB m), −70.8 (I, AB m), −83.8 (A, AB m), −84.5 (N, AB m), −86.5 (O, AB m), −89.8 (J, AB m), −92.4 (K, AB m), −99.3 (B AB m), −105.7 (M, m), −110.7 (E, m), −130.0 (C, AB m), 133.7 (L, brs), −138.4 (D, AB m). J_{AB} = 175 Hz, J_{CD} = 246 Hz, J_{FG} = 156 Hz, J_{HI} = 181 Hz, J_{JK} = 174 Hz, J_{NO} = 130 Hz, J_{PQ} = 153.3 Hz, $J_{P(NO)}$ = 10.4 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 454 (M^+ − F), 3.8; 438 (M^+ − Cl), 3.4; 330 (M^+ − OSF_5), 31.4; 314 ($C_6F_{12}N^+$), 11.5; 280 (M^+ − CF_2OSF_5), 26.5; 264 (M^+ − $CFClOSF_5$), 4.4; 259 ($CF_2CFClOSF_5{}^+$) 2.0; 230 ($C_4F_8NO^+$), 3.9; 214 ($C_4F_8N^+$), 1.1; 195 ($C_4F_7N^+$), 0.6; 176 ($C_4F_6N^+$), 7.5; 164 ($C_3F_6N^+$), 0.6; 145 ($C_3F_5N^+$), 3.7; 135 ($C_2F_4Cl^+$), 17.9; 127 ($SF_5{}^+$), 100; 119 ($C_2F_5{}^+$), 9.5; 114 ($C_2F_4N^+$), 2.9; 105 (SF_3O^+), 26.2; 100 ($C_2F_4{}^+$), 10.6; 89 ($SF_3{}^+$), 7.2; 85 (CF_2Cl^+), 8.9; 69 ($CF_3{}^+$), 20.9; 67 (SFO^+), 1.3. Anal. Calcd for $C_6F_{16}ClNOS$: C, 15.22; F, 64.2. Found: C, 15.34; F, 64.2.

Properties of $CF_2CF_2OCF_2CF_2NCF(OSF_5)CF_2Cl$ (31) and $CF_2CF_2OCF_2CF_2NCFClCF_2OSF_5$ (32). A mixture of isomers containing 44 parts of **31** and 56 parts of **32** is obtained in 51% yield in a trap at −10 °C. Spectral data obtained for this mixture are as follows. IR (cm^{-1}): 1403 w, 1332 vs, 1301 s, 1218 vs, 1190 s, 1142 s, 1085 m, 1035 m, 919 s, br, 872 ms, br, 816 ms, br, 793 mw, 775 m, 759 m, 740 w, 722 w, 671 mw, 643 w, 622 mw, 599 m, 576 w, 489 mw. NMR: $[CF_2{}^ACF_2{}^BCF_2{}^BCF_2{}^ANCF^C(OSF_4{}^DF^E)CF_2{}^FCl]$ and $[CF_2{}^ACF_2{}^BCF_2{}^BCF_2{}^ANCF^GClCF_2{}^HOSF_4{}^IF^J]$: ^{19}F, δ 73.9 (D, dd), 72.0 (I, dt), 61.5 (E, m), 61.1 (J, m), −70.3 (F, AB m), −83.3 (H, m), −85 to −96 (A, B, m), −102.7 (G, m), −107 (C, m). J_{CD} = 14.1 Hz, J_{DE} = 157 Hz, J_{IJ} = 154 Hz, J_{HI} = 11.3 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 470 (M^+ − F), 1.0; 454 (M^+ − Cl), 0.5; 346 (M^+ − OSF_5), 13.0; 330 ($C_6F_{12}NO^+$), 2.5; 296 (M^+ − CF_2OSF_5), 9.8; 280 (M^+ − $CFClOSF_5$), 5.5; 259 ($CF_2CFClOSF_5{}^+$), 0.6; 230 ($C_4F_8NO^+$), 1.6; 192 ($C_4F_6NO^+$), 8.9; 180 ($C_3F_6NO^+$), 6.3; 164 ($C_3F_6N^+$), 5.8; 135 ($C_2F_4Cl^+$), 21.6; 127 ($SF_5{}^+$), 100; 119 ($C_2F_5{}^+$), 52.6; 114 ($C_2F_4N^+$), 14.3; 105 (SF_3O^+), 12.8; 100 ($C_2F_4{}^+$), 20.4; 89 ($SF_3{}^+$), 2.5; 85 (CF_2Cl^+), 12.3; 69 ($CF_3{}^+$), 20.4; 67 (SFO^+), 1.0. Anal. Calcd for $C_6F_{16}ClNO_2S$: F, 62.1. Found: F, 60.9.

(b) Trifluoromethyl Hypofluorite/chlorite. The perfluorovinylamine (A, B, C, or D) (5 mmol) and trifluoromethyl hypohalite (6 mmol) are condensed into a 30-mL stainless steel Hoke cylinder at −196 °C and allowed to warm slowly to 25 °C. The products are then separated by trap-to-trap distillation. Volatile compounds from the trap at −85 and −110 °C are combined and purified by gas chromatography by using a Kel-F No. 90 column (4 m) at 100 °C.

Properties of $(CF_3)_2NCF_2CF_2OCF_3$ (33). Compound **33** is obtained as the only addition isomer from the reaction of the perfluorovinylamine C with CF_3OF. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1375 s, 1350 vs, br, 1293 s, 1250 vs, 1225 vs, 1198 s, 1155 vs, 1100 w, 1072 vw, 998 s, 932 m, 884 m, 857 w, 830 w, 772 m, 737 m, 665 vw, 650 vw. NMR $[(CF_3{}^A)_2NCF_2{}^BCF_2{}^COCF_3{}^D]$: ^{19}F, δ −53.0 (A, tt), −55.9 (D, t), −88.9 (C, q sept), −96.5 (B, sept). J_{AB} = 14.9 Hz, J_{CD} = 8.7 Hz, J_{AC} = 6.2 Hz. MS EI [*m/e* (species), intensity]: 252 (M^+ − OCF_3), 1.7; 230 ($C_4F_8NO^+$), 13.6; 214 ($C_4F_8N^+$), 1.7; 202 ($(CF_3)_2NCF_2{}^+$), 14.4; 164 ($C_3F_6N^+$), 11.9; 135 ($CF_3OCF_2{}^+$), 3.4; 119 ($C_2F_5{}^+$), 23.7; 114 ($C_2F_4N^+$), 35.6; 100 ($C_2F_4{}^+$), 2.5; 69 ($CF_3{}^+$) 100.

Properties of $CF_2CF_2CF_2CF_2NCF_2CF_2OCF_3$ (34). Fractionation of the reaction mixture gives a 6.4% yield of **34** from the reaction of the perfluorovinylamine A with CF_3OF. The other addition isomer is not isolated. However, other products obtained in the −196 °C trap are CF_4 and COF_2. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1898 w, 1345 s, 1310 s, 1293 s, 1252 vs, 1230 vs. 1178 s, 1153 vs, 1079 m, 1030 m, 980 s, 904 m, 873 w, 839 w, 797 s, 682 w, 614 w, 563 w. NMR $[CF_2{}^ACF_2{}^BCF_2{}^BCF_2{}^ANCF_2{}^CCF_2{}^DOCF_3{}^E]$: ^{19}F, δ −55.9 (E, t), −89.5 (D, m), −91.3 (B, m), −97.7 (C, p), −133.2 (A, br s). J_{BC} = 12.4 Hz, J_{BD} = 7.4 Hz, J_{DE} = 8.7 Hz. MS EI [*m/e* (species), intensity]: 380 (M^+ − F), 8.1; 330 (M^+ − CF_3), 2.2; 314 (M^+ − OCF_3), 11.8; 264 (M^+ − CF_2OCF_3), 100; 214 ($C_4F_8N^+$), 16.2; 176 ($C_4F_6N^+$), 17.6; 164 ($C_3F_6N^+$), 6.6; 150 ($C_3F_6{}^+$), 7.4; 145 ($C_3F_5N^+$), 6.6; 119 ($C_2F_5{}^+$), 54.4; 114 ($C_2F_4N^+$), 14.7; 100 ($C_2F_4{}^+$), 20.6; 69 ($CF_3{}^+$), 74.4.

Properties of $CF_2CF_2OCF_2CF_2NCF_2CF_2OCF_3$ (35). Compound **35** is obtained as the only addition isomer from the reaction of the perfluorovinylamine B with CF_3OF. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1370 sh,w, 1310 s, 1300 s, 1243 vs, 1233 vs, 1198 s, 1183 s, 1152 s, 1110 m, 1069 m, 933 s, 907 m, 838 w, 793 s, 742 w, 709 w, 684 w, 670 m, 655 w, 627 m, 530 w, 499 w. NMR $[CF_2{}^ACF_2{}^BOCF_2{}^BCF_2{}^ANCF_2{}^CCF_2{}^DOCF_3{}^E]$: ^{19}F, δ −55.9 (E, t), −87.6 (A, br s), −90.7 (D, m), −92.9 (B, tt), −96.3 (C, p). J_{BC} = 17.3 Hz, J_{BD} = 9.3 Hz, J_{DE} = 8.78 Hz. MS EI [*m/e* (species), intensity]: 396 (M^+ − F) 1.7; 330 (M^+ − OCF_3), 1.9; 308 (M^+ − CF_5), 1.9; 280 (M^+ − CF_2OCF_3), 25.9; 230 ($C_4F_8NO^+$), 1.9; 192 ($C_4F_6NO^+$), 5.6; 164 ($C_3F_6N^+$), 13.0; 119 ($C_2F_5{}^+$), 100; 114 ($C_2F_4N^+$), 35.2; 100 ($C_2F_4{}^+$), 44.4; 69 ($CF_3{}^+$), 74.1. Anal. Calcd for $C_7F_{15}NO_2$: C, 20.24; F, 68.7. Found: C, 20.44; F, 68.5.

Properties of $\overline{CF_2CF_2CF_2CF_2CF_2N}CF_2CF_2OCF_3$ (36). This compound is obtained as the only addition isomer from the reaction of the perfluorovinylamine **D** with CF_3OF. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1372 m, 1345 sh, 1332 vs, 1293 s, 1278 s, 1249 vs, 1217 vs, 1210 sh, 1172 s, 1158 s, 1134 s, 1074 m, 1020 m, 976 s, 903 w, 851 vw, 838 vw, 789 m, 692 vw, 660 vw, 645 w, 635 w, 589 vw, 515 vw, 490 vw. NMR [$\overline{CF_2{}^{A}CF_2{}^{B}CF_2{}^{C}CF_2{}^{B}CF_2{}^{A}N}CF_2{}^{D}CF_2{}^{E}OCF_3{}^{F}$]: ^{19}F, δ −56.0 (F, t) −90.7 (E, m), −91.8 (C, br s), −132.6 (B, m), −134.7 (A, m). J_{CD} = 9.8 Hz, J_{EF} = 8.7 Hz. MS EI [*m/e* (species), intensity]: 430 ($M^+ - F$), 2.5; 380 ($M^+ - CF_3$), 1.0; 364 ($M^+ - OCF_3$), 3.1; 314 ($C_6F_{12}N^+$), 41.7; 264 ($C_5F_{10}N^+$), 5.8; 226 ($C_5F_8N^+$), 14.6; 185 ($C_2F_4OCF_3{}^+$), 1.0; 176 ($C_4F_6N^+$), 3.9; 169 ($C_3F_7{}^+$), 2.9; 164 ($C_3F_6N^+$), 3.9; 145 ($C_3F_5N^+$), 3.9; 135 ($CF_2OCF_3{}^+$), 3.9; 131 ($C_3F_5{}^+$), 14.6; 119 ($C_2F_5{}^+$), 72.8; 114 ($C_2F_4N^+$), 14.6; 100 ($C_2F_4{}^+$), 27.2; 69 ($CF_3{}^+$), 100. Anal. Calcd for $C_8F_{17}NO$: C, 21.38; F, 71.9. Found: C, 21.31; F, 71.6.

Preparation and Properties of $\overline{CF_2CF_2CF_2CF_2N}CFClCF_2OCF_3$ (37). CF_3OCl (1.2 mmol), purified by trap-to-trap distillation prior to use, is condensed onto 1 mmol of perfluorovinylamine **A** in a 30-mL stainless steel Hoke reactor at −196 °C. After the reaction vessel warms slowly to 25 °C over a period of 24 h, the products are separated by trap-to-trap distillation. Compound **37** is obtained in 61% yield in a trap at −25 °C along with a trace amount of the isomer. Spectral data for this compound are as follows. IR (gas) (cm^{-1}): 1402 w, 1342 vs,br, 1289 vs, 1245 vs, 1227 vs, 1178 vs, 1151 vs, 1078 ms, 1038 m, 1024 ms, 977 vs, 888 w, 849 mw, 827 w, 802 ms, 778 w, 752 ms, 721 w, 675 mw, 643 mw, 610 mw, 560 w. NMR [$\overline{CF_2{}^{AB}CF_2{}^{C}CF_2{}^{C}CF_2{}^{AB}N}CFCl^{D}CF_2{}^{EF}OCF_3{}^{G}$]: ^{19}F, δ −55.8 (G, t), −85.5 (E, AB m), −86.9 (F, AB m), −89.4 (A, AB m), −91.6 (B, AB m), −106.5 (D m), −132.9 (C, br s). J_{AB} = 175 Hz, J_{EF} = 137 Hz, $J_{(EF)G}$ = 7.6 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 396 ($M^+ - F$), 40.8; 380 ($M^+ - Cl$), 55.0; 330 ($M^+ - OCF_3$), 46.1; 314 ($C_6F_{12}N^+$), 10.3; 295 ($C_6F_{11}N^+$), 12.5; 280 ($C_4F_8NCFCl^+$), 44.8; 276 ($C_6F_{10}N^+$), 42.5; 264 ($C_5F_{10}N^+$), 11.7; 201 ($M^+ - C_4F_8N$), 33.1; 176 ($C_4F_6N^+$), 14.8; 135 ($C_2F_4Cl^+$), 53.4; 119 ($C_2F_5{}^+$) 17.3; 100 ($C_2F_4{}^+$), 19.5; 95 ($C_2F_3N^+$), 13.8; 85 (CF_2Cl^+), 12.0; 81 ($C_2F_3{}^+$), 14.8; 69 ($CF_3{}^+$), 100.

(c) Perfluoro-*tert*-butyl Hypochlorite. Into a dry Pyrex glass reactor at −196 °C fitted with a Kontes Teflon stopcock are condensed 1.1 mmol of $(CF_3)_3COCl$ and 1 mmol of the perfluorovinylamine **A** or **B**. The reaction vessel is warmed slowly to 25 °C over a period of 16 h and the products are separated by trap-to-trap distillation.

Properties of $\overline{CF_2CF_2CF_2CF_2N}CF[OC(CF_2)_3]CF_2Cl$ (38). Compound **38** is obtained as a colorless liquid in 47% yield in a trap cooled at −20 °C. It has limited solubility in $CDCl_3$, CH_2Cl_2, and $CFCl_3$ at 25 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1349 s, 1283 vs, 1228 vs, 1207 ms, 1176 sh, 1136 s, 1074 vw, 1030 ms, 997 ms, 978 s, 872 vw, 801 mw, 772 vw, 732 mw, 709 w, 676 w, 615 w, 560 w. NMR (298 K): [$\overline{CF_2{}^{AB}CF_2{}^{CD}CF_2{}^{CD}CF_2{}^{AB}N}CF^{E}[OC(CF_3)_3{}^{F}]CF_2{}^{GH}Cl$]: ^{19}F, δ −68.0 (G, Ab m), −69.3 (H, AB m), −69.9 (F, d), −82.4 (A, AB m), −98.5 (B, vbr, $\Delta\nu_{1/2} = \sim$1KHz), −108.6 (E, m), −129.1 (C, AB m), −137.5 (D, AB m). J_{CD} = 248 Hz, J_{GH} = 176 Hz, J_{EF} = 11.4 Hz. NMR (at 246 K): [$\overline{CF^{A}F^{B}CF^{C}F^{D}CF^{E}F^{F}CF^{G}F^{H}N}CF^{I}[OC(CF_3)_3{}^{J}]CF_2{}^{KL}Cl$]: ^{19}F, δ −68.3 (K, AB m), −69.6 (J, d), −70.5 (L, AB m), −79.4 (A, AB d), −81.5 (B, AB d), −91.8 (G, AB d), −108 (H, AB d), −109.2 (I, m), −125.0 (C, AB d), −130.5 (D, AB d), −136.3 (E, AB d), −140.1 (F, AB d). J_{AB} = 170 Hz, J_{CD} = 175 Hz, J_{EF} = 249 Hz, J_{GH} = 242 Hz, J_{KL} = 175 Hz, J_{IJ} = 8.2 Hz. ΔG^* and k_c from variable temperature NMR (arbitrary fluorine labelling): [A, H] T_c = 266 K, ΔG^* = 11.71 kcal mol^{-1}, k = 1281 s^{-1}; [B, G broad hump at 292 K] T_c = 292 K, ΔG^* = 11.7 kcal mol^{-1}, k = 10514 s^{-1}; [C, D, E, F], T_c = 282 K, ΔG^* = 11.91, 12.12 kcal mol^{-1}, k = 3419, 2371 s^{-1}, respectively. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 546 ($M^+ - F$), 12.6; 530 ($M^+ - Cl$), 10.1; 480 ($M^+ - CF_2Cl$), 43.4; 351 ($M^+ - C_4F_8N$), 100; 335 ($C_6F_{13}O^+$), 23.1; 330 ($C_6F_{11}NCl^+$), 16.7; 314 ($C_6F_{12}N^+$), 1.4; 280 ($C_4F_8NCFCl^+$), 4.0; 264 ($C_5F_{10}N^+$), 3.0; 235 ($C_4F_9O^+$), 2.9; 219 ($C_4F_9{}^+$), 6.6; 197 ($C_4F_7O^+$), 2.9; 181 ($C_4F_7{}^+$), 11.2; 135 ($C_2F_4Cl^+$), 15.3; 131 ($C_3F_5{}^+$), 23.2; 119 ($C_2F_5{}^+$), 4.5; 100 ($C_2F_4{}^+$), 9.7; 97 ($C_2F_3O^+$), 9.6; 85 (CF_2Cl^+), 23.3; 81 ($C_2F_3{}^+$), 11.0; 69 ($CF_3{}^+$), 99.0.

Properties of $\overline{CF_2CF_2OCF_2CF_2N}CFClCF_2OC(CF_3)_3$ (39). This compound is obtained as a colorless liquid in 51% yield in a trap at −20 °C. Its solubility properties resemble compound **38**. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1331 m, 1285 vs, 1226 vs, 1200 m, 1185 ms, 1147 ms, 1109 m, 1055 w, 998 w, 980 w, 934 w, 908 vw, 837 w, 813 vw, 794 w, 755 vw, 732 w. NMR [$\overline{CF_2{}^{AB}CF_2{}^{CD}OCF_2{}^{CD}CF_2{}^{AB}N}CFCl^{E}CF_2{}^{FG}OC(CF_3)_3{}^{H}$]: ^{19}F, δ −70.3 (H, t), −81.5 (F, AB m), −83.4 (G, AB m), −86.2 (C, AB m), −87.1 (D, AB m), −89.2 (A, AB m), −92.2 (B, AB m), −102.5 (E m). J_{AB} = 195 Hz, J_{CD} = 152 Hz, J_{FG} = 128 Hz, $J_{(FG)H}$ = 9.4 Hz; MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 562 ($M^+ - F$), 18.7; 546 ($M^+ - Cl$), 40.3; 496 ($M^+ - CF_2Cl$), 14.5; 351 ($M^+ - C_4F_8NO$), 100; 335 ($C_6F_{13}O^+$), 22.0; 296 ($C_4F_8NOCFCl^+$), 25.6; 285 ($C_5F_{11}O^+$), 8.3; 235 ($C_4F_9O^+$) 4.5; 219 ($C_4F_9{}^+$), 8.1; 181 ($C_4F_7{}^+$), 14.6; 180 ($C_3F_6NO^+$), 6.5; 164 ($C_3F_6N^+$), 6.2; 135 ($C_2F_4Cl^+$), 18.3; 131 ($C_3F_5{}^+$), 20.2; 119 ($C_2F_5{}^+$), 67.0; 114 ($C_2F_4N^+$), 10.1; 100 ($C_2F_4{}^+$), 20.0; 97 ($C_2F_3O^+$), 13.6; 85 (CF_2Cl^+), 11.6; 69 ($CF_3{}^+$), 99. Anal. Calcd for $C_{10}F_{20}ClNO_2$: C, 20.64; F, 65.4. Found: C, 20.70; F, 65.1.

Photolytic Reactions of Perfluorovinylamines. (a) Reaction with Pentafluorosulfur Chloride. Into a quartz vessel fitted with a Kontes Teflon stopcock are condensed purified pentafluorosulfur chloride (1.1 mmol) and 1 mmol of the perfluorovinylamine **A** or **B** at −196 °C. After warming the reaction mixture is warmed to 25 °C, it is photolyzed at 3000 Å for 16–18 h. The products are then separated by trap-to-trap distillation. The other products identified from this reaction are the vinylamine–chlorine adduct, S_2F_{10}, and an unidentified nonvolatile residue.

Properties of $\overline{CF_2CF_2CF_2CF_2N}CF(SF_5)CF_2Cl$ (40). This compound is obtained as a low volatile colorless liquid in 54% yield in a trap at −15 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1337 s, 1292 ms, 1253 s, 1228 vs, 1192 s, 1151 m, 1124 ms, 1088 m, 1040 ms, 977 vs, 927 w, 897 vs, 879 ms, 823 m, 780 ms, 742 ms, 683 s, 651 w, 600 m, 582 mw, 560 w, 482 mw, 430 m, 406 w. NMR [$\overline{CF_2{}^{A}CF_2{}^{B}CF_2{}^{B}CF_2{}^{A}N}CF^{C}(SF_4{}^{D}F^{E})CF_2{}^{F}Cl$]: ^{19}F, δ 65.3 (E, m), 48.7 (D, brd), −63.3 (F, AB m), ∼−90 (A, complex m), −121.4 (C, m), ∼−133 (B, complex m). J_{DE} = 143.4 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 438 ($M^+ - F$), 3.8; 330 ($M^+ - SF_5$), 52.9; 314 ($C_6F_{12}N^+$), 9.2; 295 ($M^+ - SF_5Cl$), 9.9; 276 ($C_6F_{10}N^+$), 33.0; 226 ($C_5F_8N^+$), 1.5; 196 ($C_4F_7NH^+$), 1.9; 176 ($C_4F_6N^+$), 8.1; 164 ($C_3F_6N^+$), 0.4; 145 ($C_3F_5N^+$), 3.2; 135 ($C_2F_4Cl^+$), 17.3; 127 ($SF_5{}^+$), 2.4; 119 ($C_2F_5{}^+$), 6.6; 114 ($C_2F_4N^+$), 2.1; 100 ($C_2F_4{}^+$), 9.2; 69 ($CF_3{}^+$), 4.

Properties of $\overline{CF_2CF_2OCF_2CF_2N}CF(SF_5)CF_2Cl$ (41). This compound is obtained as a slightly volatile colorless liquid in 51% yield in a trap at −15 °C. Spectral data obtained are as follows. IR (cm^{-1}): 1328 m, 1267 sh, 1196 vs,br, 1123 mw, 1083 w, 1058 ms, 1030 mw, 1007 w, 980 mw, 931 mw, 886 m, 812 mw, 778 m, 742 m, 683 w, 670 vw, 659 vs, 624 m, 596 ms, 563 m, 537 mw, 488 w. NMR [$\overline{CF_2{}^{A}CF_2{}^{B}OCF_2{}^{B}CF_2{}^{A}N}CF^{C}(SF_4{}^{D}F^{E})CF_2{}^{F}Cl$]: ^{19}F, δ 66.1 (E, m), 48.9 (D, brd), −59.9 (F, AB m), −82 to −95 (A,B complex AB m), −117.5 (C, m). J_{DE} = 141.5 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 454 ($M^+ - F$), 0.1; 346 ($M^+ - SF_5$), 24.3; 330 ($C_6F_{12}NO^+$), 2.3; 311 ($M^+ - SF_5Cl$), 24.9; 292 ($C_6F_{10}NO^+$), 86.6; 264 ($C_5F_{10}N^+$), 0.8; 213 ($C_4F_7NO^+$), 0.8; 197 ($C_4F_7O^+$), 1.7; 195 ($C_4F_7N^+$), 1.7; 176 ($C_4F_6N^+$), 1.6; 164 ($C_3F_6N^+$), 5.9; 147 ($C_3F_5O^+$), 5.0; 145 ($C_3F_5N^+$), 26.6; 131 ($C_3F_5{}^+$), 1.1; 127 ($SF_5{}^+$), 0.8; 119 ($C_2F_5{}^+$), 49.7; 114 ($C_2F_4N^+$), 2.5; 100 ($C_2F_4{}^+$), 16.3; 89 ($SF_3{}^+$), 100; 69 ($CF_3{}^+$), 58. Anal. Calcd for $C_6F_{16}ClNOS$: C, 15.21; F, 64.2. Found: C, 15.09; F, 62.6.

(b) Reaction with *N*-Chlorobis(trifluoromethyl)amine. In a quartz vessel at −196 °C fitted with a Kontes Teflon stopcock, 1.1 mmol of $(CF_3)_2NCl$ is condensed onto 1 mmol of the perfluorovinylamine **A** or **B**. After the reaction mixture is warmed to 25 °C and photolysis is performed at 3000 Å for 16–18 h, the products are separated by trap-to-trap distillation. The order products identified from this reaction are the chlorine adduct and tetrakis(trifluoromethyl)hydrazine.

Properties of $\overline{CF_2CF_2CF_2CF_2N}CF[N(CF_3)_2]CF_2Cl$ (42). This compound is obtained as a slightly volatile colorless liquid in 40% yield in a trap at −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1348 vs, 1307 s, 1283 ms, 1265 s, 1228 vs, 1166 ms, 1143 m, 1126 m, 1082 m, 1041 ms, 988 ms, 940 w, 886 w, 823 mw, 773 mw, 761 w, 723 m, 677 vw, 658 vw, 613 w, 583 w, 555 mw. NMR [$\overline{CF_2{}^{AB}CF_2{}^{CD}CF_2{}^{CD}CF_2{}^{AB}N}CF^{E}[N(CF_3{}^{F})_2]CF_2{}^{GH}Cl$]: ^{19}F, δ −51.1 (F, dm), −59.3 (G, AB m), −61.1 (H, AB m), −88.0 (A, AB m), −93.3 (B, AB m), −105.0 (E, m), −131.7 (C, AB m), 135.5 (D, AB m). J_{AB} = 168 Hz, J_{CD} = 244 Hz, J_{EF} = 15.1 Hz, J_{GH} = 176 Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 463 ($M^+ - F$), 3.8; 447 ($M^+ - Cl$), 4.8; 397

($M^+ - CF_2Cl$), 10.9; 330 ($M^+ - (CF_3)_2N$), 70.8; 314 ($C_6F_{12}N^+$), 24.1; 309 ($M^+ - C_2F_6 - Cl$), 17.1; 280 ($C_4F_8NCFCl^+$), 6.1; 268 ($M^+ - C_4F_8N$), 73.3; 214 ($C_4F_8N^+$), 15.9; 196 ($C_4F^7NH^+$), 12.0; 195 ($C_4F_7N^+$), 3.6; 180 ($C_3F_5NCl^+$), 20.7; 176 ($C_4F_6N^+$), 14.9; 145 ($C_3F_5N^+$), 10.5; 135 ($C_2F_4Cl^+$), 13.0; 131 ($C_3F_5^+$), 7.2; 119 ($C_2F_5^+$), 11.1; 114 ($C_2F_4N^+$), 35.4; 100 ($C_2F_4^+$), 10.8; 85 (CF_2Cl^+), 8.1; 69 (CF_3^+), 100. Anal. Calcd for $C_8F_{17}ClN_2$: C, 19.9; F, 67.0. Found: C, 20.0; F, 67.2.

Properties of $\overline{CF_2CF_2OCF_2CF_2N}CF[N(CF_3)_2]CF_2Cl$ (43). This compound is obtained as a low volatile colorless liquid in 42% yield in a trap at −20 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1348 vs, 1306 s, 1236 vs, 1226 sh, 1202 ms, 1148 ms, 1130 m, 988 mw, 954 w, 930 m, 865 mw, 831 w, 798 vw, 774 mw, 742 m, 724 mw, 668 mw, 624 w, 487 w. NMR [$\overline{CF_2^ACF_2^{BC}OCF_2^{BC}OCF_2^AN}CF^D[N(CF_3^E)_2]CF_2^F$-Cl]: ^{19}F, δ −51.0 (E, dm), −63.12 (F, AB m), −87.0 (B, AB m), −87.5 (C, AB m), −92.4 (A, brs), −109.2 (D, m). $J_{BC} = 156$ Hz. MS CI [*m/e* (species), intensity] (correct isotopic ratio is observed): 479 ($M^+ - F$), 1.1; 463 ($M^+ - Cl$), 1.3; 413 ($M^+ - CF_2Cl$), 5.1; 346 ($M^+ - (CF_3)_2N$), 34.9; 330 ($C_6F_{12}NO^+$), 7.3; 325 ($M^+ - C_2F_6 - Cl$), 7.4; 292 ($C_6F_{10}NO^+$), 9.5; 268 ($M^+ - C_4F_8N$), 76.1; 230 ($C_4F_8NO^+$), 0.4; 214 ($C_4F_8N^+$), 14.2: 192 ($C_4F_6NO^+$), 10.1; 180 ($C_3F_5NCl^+$), 24.2; 164 ($C_3F_6N^+$), 14.6; 145 ($C_3F_5N^+$), 10.8; 119 ($C_2F_5^+$), 32.0; 114 ($C_2F_4N^+$), 25.6; 100 ($C_2F_4^+$), 12.9, 95 ($C_2F_3N^+$), 11.8; 85 (CF_2Cl^+), 10.8; 83 (CF_3N^+), 11.9; 69 (CF_3^+), 100.

Acknowledgment. A.V., R.L.K., and J.M.S. are grateful for the support of the National Science Foundation (CHE-9003509), and Air Force Office of Scientific Research (91-0189). R.L.K. thanks the Science and Technology Agency of Japan and the Government Industrial Research Institute, Nagoya, Japan, for financial support. We thank Dr. Gary Knerr for variable-temperature NMR and mass spectral data.