Inorg. Chem. **1992**, *31*, 4917–4920

Perfluoro- and Polyfluoroazaalkenes as Precursors to Bis(perfluoroalkyl or polyfluoroalkyl) Alkyl (or Aryl) Tertiary Amines

Yihong Chen, Nimesh R. Patel, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

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

Received July 20, 1992

Upon thermolysis the olefins $CF_2{=}CFX$ (X = Cl, F) readily insert into one of the nitrogen chlorine bonds of $C_3F_7NCl_2$ to form $C_3F_7N(Cl)CF_2CFCl_2$ (**1**) and $C_3F_7N(Cl)CF_2CF_2Cl$ (**2**). Photolysis of both **1** and **2** at 3000 Å gives the perfluoroazaalkene $C_3F_7N{=}CF_2$ with concomitant loss of $CFXCl_2$. With either $(C_6H_5)_3P$ or CsCl, **1** and **2** give the more highly substituted azaalkenes $C_2F_5CF{=}NCF_2CFCl_2$ and $C_2F_5CF{=}NCF_2CF_2Cl$, respectively. Cyanogen chloride readily inserts into the N–Cl bond of **1** to form a reactive carbimide, $C_3F_7(N{=}CCl_2)CF_2CFCl_2$. Azaalkenes in the presence of AgF in CH_3CN or C_6H_5CN can be reacted with a variety of alkyl iodides, phenyl iodide, and di- and tetrabromoethanes to give bis(perfluoroalkyl) alkyl (or aryl) tertiary amines and highly substituted ethanes; e.g., for $R_fN(R)CF_3$, when $R_f = CF_3$, C_2F_5, and C_3F_7, R = CH_3, C_2H_5, C_6H_5, $(CH_3)_3Si$, CF_3S; CH_3, C_2H_5; CH_3; and CH_3, respectively. With $CF_3N{=}CF_2$ and AgF, $BrCH_2CH_2Br$ and $Br_2CHCHBr_2$ give $(CF_3)_2NCH_2CH_2N(CF_3)_2$ and $[(CF_3)_2N]_2CHCH[N(CF_3)_2]_2$, respectively. Methyl iodide with $(CF_3)_2NN{=}CFN(CF_3)N(CF_3)_2$ and $SF_5N{=}C(Cl)C_2F_5$ in the presence of AgF form $(CF_3)_2NN(CH_3)CF_2N(CF_3)N(CF_3)_2$ and $SF_5N(CH_3)CF_2CF_2CF_3$. Unexpectedly, $C_3F_7N{=}CF_2$ with CF_3CH_2I and AgF at 100 °C results in $C_2F_5CF{=}NCH_2CF_3$. These mixed bis(perfluoroalkyl) alkyl(or aryl) tertiary amines are stable materials whose thermodynamic and physical properties suggest possible real world applications.

Introduction

Studies of the chemistry of the nitrogen–halogen bond continue to provide a variety of new routes to a range of compounds of varying properties. These materials in turn are viable precursors to mixed perfluoroalkyl alkyl(or aryl) tertiary amines which exhibit attractive thermal stabilities and vapor pressures.

Insertion of olefins $CF_2{=}CFX$ (X = Cl, F) into the nitrogen–chlorine bonds of dichloro(perfluoroalkyl)amines, R_fNCl_2, occurs readily, providing a high-yield, straightforward route to secondary (polyfluoroalkyl or perfluoroalkyl)chloroamines and tertiary (polyfluoroalkyl or perfluoroalkyl)amines. At 65–70 °C, insertion into only one of the nitrogen–chlorine bonds occurs to give $R_fN(CF_2CFXCl)Cl$, while, at 90–100 6C, insertion into both nitrogen–chlorine bonds produces the tertiary amines $R_fN(CF_2CFXCl)_2$ in good yields.[1-3] Olefins insert with equal ease into the N–X bond of $CF_2{=}NX$ (X = Cl, Br).[4,5]

Advantage has been taken of the ready thermal or photolytic activation of the N–Cl bond, particularly in the secondary chloroamines, to insert nitriles to form carbimides in high yields, viz.

$$R_f(CF_3)NCl + RC{\equiv}N \xrightarrow{h\nu} R_f(CF_3)NN{=}CClR^{6-9}$$

$$R = Cl, CF_3;\ R_f = CF_3, CF_3CF_2, CCl_2FCF_2, CClF_2CF_2$$

The polar nature of the $-N{=}C<$ bonds allows the addition of chlorine fluoride at 25 °C to form new chloroamines which are precursors under photolytic conditions to a thermally stable family of tetrazanes,[7] e.g.

$$R_f(CF_3)NN{=}CClR + ClF \rightarrow R_f(CF_3)NN(Cl)CClFR$$

$$R_f(CF_3)NN(Cl)CClFR \xrightarrow[-Cl_2]{h\nu} [R_f(CF_3)NNCClFR]_2$$

Interestingly, when certain secondary bis(perfluoro- or polyfluoroalkyl)chloroamines are photolyzed neat, rather than dimerizing to form hydrazines and chlorine, essentially quantitative yields of perfluoroazaalkenes and chlorofluorocarbons result.[1,10]

$$R_fN(CF_2CFXCl)Cl \xrightarrow{h\nu} R_fN{=}CF_2 + CFXCl_2$$

Dechlorofluorination of certain secondary chloroamines with triphenylphosphine also gives rise to azaalkenes.[10]

$$CF_3N(CF_2CFXCl)Cl + (C_6H_5)_3P \rightarrow CF_3N{=}CFCFXCl + (C_6H_5)_3PClF$$

In the work described here, we have extended the reaction chemistry of $C_3F_7NCl_2$. Additionally, we report the utilization of the silver derivatives of azaalkenes as intermediates in the formation of a variety of perfluoroalkyl alkyl (or aryl) tertiary amines.

Results and Discussion

A large number of *N*-chloro(perfluoroalkyl)(polyfluoroalkyl)amines can be photolytically induced to lose chlorofluorocarbons to form perfluoroazaalkenes, $R_fN{=}CF_2$.[1-3,8] The parent chloroamines are readily obtained via the saturation of the carbon–nitrogen triple bond in perfluoroalkane nitriles with chlorine fluoride, followed by insertion of a variety of perfluoro- and polyfluoroolefins into one of the resulting nitrogen–chlorine bonds. For example, new in this report are the olefin insertion reactions with $C_3F_7NCl_2$:

---

[1] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 2187 and references therein.

[2] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Heteroatom Chem.* **1990**, *1*, 167.

[3] Zheng, Y. Y.; Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1992**, *31*, 488.

[4] Bauknight, C. W., Jr.; DesMarteau, D. D. *J. Org. Chem.* **1988**, *53*, 4443.

[5] Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 4844.

[6] Dobbie, R. C.; Emeléus, H. J. *J. Chem. Soc.* **1964**, A933.

[7] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 3345 and references therein.

[8] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1990**, *29*, 4255 and references therein.

[9] Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. *J. Fluorine Chem.* **1990**, *40*, 395 and references therein.

[10] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1990**, *29*, 571 and references therein.

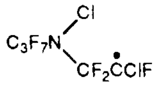
0020-1669/92/1331-4917$03.00/0

$$C_2F_5CN + ClF \xrightarrow{-78\ ^\circ C} C_3F_7NCl_2$$

$$C_3F_7NCl_2 + CF_2{=}CFCl \xrightarrow{\Delta} \underset{\textbf{1}\ (75\%)}{C_3F_7N(Cl)CF_2CFCl_2}$$

$$C_3F_7NCl_2 + CF_2{=}CF_2 \xrightarrow{\Delta} \underset{\textbf{2}\ (40\%)}{C_3F_7N(Cl)CF_2CF_2Cl}$$

These chloroamines are purified via trap-to-trap distillation. Only a single isomer of **1** is obtained in a yield nearly twice that of the insertion compound **2**. Given the bulky nature of the radical $C_3F_7\dot{N}Cl$, it is not surprising that the predominant intermediate in the reaction with $CF_2{=}CClF$ is formed by attack at the carbon bonded to two fluorine atoms



which minimizes the steric interaction between the two chlorine atoms. Photolysis of **1** or **2** at 3000 Å in a quartz vessel gives the perfluoroazaalkene in nearly quantitative yield:

$$C_3F_7N(Cl)CF_2CFXCl \xrightarrow[-CFXCl_2]{h\nu} C_3F_7N{=}CF_2$$

It is interesting to note that more highly substituted azaalkenes result when **1** or **2** is reacted with $(C_6H_5)_3P$[10] or with CsCl

$$\textbf{1} + (C_6H_5)_3P \text{ or } CsCl \xrightarrow{CH_3CN} \underset{\textbf{3}\ (77\%)}{C_2F_5CF{=}NCF_2CFCl_2} + (C_6H_5)_3PClF\ (Cl_2 + CsF)$$

$$\textbf{2} + (C_6H_5)_3P \text{ or } CsCl \xrightarrow{CH_3CN} \underset{\textbf{4}\ (40\%)}{C_2F_5CF{=}NCF_2CF_2Cl} + (C_6H_5)_3PClF\ (Cl_2 + CsF)$$

Although the reaction of **2** with $(C_6H_5)_3P$ gives **4**, a second product which exhibits an infrared stretching band at 1703 cm^{-1} (assigned to C=N) was also formed but was not identified.

Insertion reactions of cyanogen chloride into the N–Cl bond of secondary chloroamines provide straightforward routes to carbimides which are also useful azaalkene precursors

$$(CF_3)_2NCl + ClCN \rightarrow (CF_3)_2NN{=}CCl_2\ [6]$$

$$\textbf{1} + ClCN \rightarrow \underset{\textbf{5}}{C_3F_7(N{=}CCl_2)CF_2CFCl_2}$$

Only a 10% yield of **5** is obtained when **1** is photolyzed with a 7-fold excess of ClCN, which is added in an attempt to reduce the formation of $C_3F_7N{=}CF_2$ and CCl_3F (90% of the products).

Chlorofluorination of carbimides with chlorine fluoride readily occurs at 25 °C. Photolysis produces polyfluoroazaalkenes and polyfluorotetrazanes.

$$(CF_3)_2NN{=}CCl_2 \xrightarrow[12\ h]{ClF} (CF_3)_2NN(Cl)CF_2Cl \xrightarrow[-Cl_2 \text{ or } -ClF]{h\nu} (CF_3)_2NN{=}CClF + [(CF_3)_2NN(CF_2Cl)]_2$$

In the presence of CsF the azaalkenes are readily dimerized.

$$(CF_3)_2NN{=}CCl_2 \text{ or } (CF_3)_2NN{=}CClF \xrightarrow{CsF} (CF_3)_2NN{=}CFN(CF_3)N(CF_3)_2$$

$$R_fN{=}CF_2 + RI \xrightarrow[CH_3CN \text{ or } C_6H_5CN]{AgF} R_fN(R)CF_3$$

R_f	R	product	yield (%)
CF_3	CH_3	**7**[11,12]	75
CF_3	C_2H_5	**8**[12]	70
C_2F_5	CH_3	**9**	67
C_2F_5	C_2H_5	**10**	40
C_3F_7	CH_3	**11**	60
$(CF_3)_2N$	CH_3	**7**[11,12]	65
CF_3	C_6H_5	**12**[13]	50
CF_3	$(CH_3)_3Si$	**13**[14]	45
CF_3	CF_3S	**14**[15]	40

Just as it is possible to take advantage of the polar nature of the nitrogen–carbon bond in an azaalkene to add chlorine fluoride, e.g., $C_3F_7N{=}CF_2 + ClF \rightarrow C_3F_7N(Cl)CF_3$ (**6**) (~100%), we now report the synthesis of a variety of tertiary amines via the reaction of silver salts formed from azaalkenes plus silver fluoride. When $R_f = C_2F_5$ or C_3F_7 in $R_fN{=}CF_2$, considerably longer reaction times were required than when $R_f = CF_3$.

Although the utilization of AgF with unsaturated compounds to form reactive nucleophiles has been employed many times before, this method is used for the first time to provide a relatively high-yield, straightforward route to bis(perfluoroalkyl) alkyl(or aryl) tertiary amines. While the synthetic routes differ, several of these tertiary amines have been in the literature for more than 20 years. For example, the fluorination of $(CH_3)_2NC(O)H$ with SF_4 in the presence of KF produces $(CH_3)_2NCF_3$ (bp 20 °C).[16,17] Surprisingly, $(CF_3)_2NCH_3$, which was produced initially by the reaction of $CF_3N{=}CF_2$ and $CH_3OSO^+SbF_6^-$,[11] boils only slightly lower at 15 °C. Substitution of CH_3 by CH_3CH_2 in **8** raises the boiling point to 30 °C, which, when coupled with its other thermodynamic properties, places it in a competitive role to replace CCl_3F in real world applications.

In place of AgF, CsF was found to work effectively for the synthesis of $(CF_3)_2NCH_3$, $(CF_3)_2NCH_2CH_3$, $(CF_3)_2NSi(CH_3)_2$, and $(CF_3)_2NSCF_3$, while the reactions do not proceed in the presence of KF or CaF_2 under analogous conditions.

This methodology can be employed equally successfully with a few more highly substituted azaalkenes, e.g.

$$(CF_3)_2NN{=}CFN(CF_3)N(CF_3)_2 + CH_3I \xrightarrow[CH_3CN]{AgF} \underset{\textbf{15}\ (55\%)}{(CF_3)_2NN(CH_3)CF_2N(CF_3)N(CF_3)_2}$$

$$SF_5N{=}C(Cl)C_2F_5\ [16] + CH_3I \xrightarrow[CH_3CN]{AgF} \underset{\textbf{16}\ (60\%)}{SF_5N(CH_3)CF_2CF_2CF_3} + \underset{\text{minor}}{SF_5N{=}CF(C_2F_5)}$$

Under analogous conditions bis[bis(trifluoromethyl)amino]ethane, $(CF_3)_2NCH_2CH_2N(CF_3)_2$ (**17**) (60% yield; bp 110 °C), and tetrakis[bis(trifluoromethyl)amino]ethane, $[(CF_3)_2N]_2CHCH[N(CF_3)_2]_2$ (**18**), were formed from the reactions of $CF_3N{=}CF_2$ with $BrCH_2CH_2Br$ and $Br_2CHCHBr_2$, respectively.

Dimerization of $CF_3N{=}CF_2$ to $(CF_3)_2NCF{=}NCF_3$ occurs readily in the presence of CsF. However, when the latter is reacted with $CH_3I/AgF/CH_3CN$, only **7** is obtained. The product formed with $(CF_3)_2NCF_2N{=}CF_2$[3] is also **7**. The formation of the single

---

[11] Henle, H.; Geisel, M.; Mews, R. *J. Fluorine Chem.* **1984**, *26*, 133.

[12] Haszeldine, R. N.; Tipping, A. E.; Valentine, R. H. *J. Fluorine Chem.* **1982**, *21*, 335.

[13] Fawcett, F. S.; Sheppard, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 4341. Hart, T. W.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1544.

[14] Ang, H. G. *J. Chem. Soc. A* **1968**, 2734.

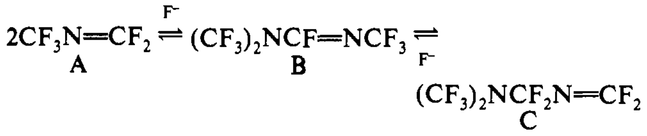
[15] Sprenger, G. H.; Shreeve, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1770.

[16] Harden, R. J.; Smith, W. C. *J. Am. Chem. Soc.* **1961**, *83*, 3422.

[17] Dmowski, W.; Kamiński, M. *J. Fluorine Chem.* **1983**, *23*, 207.

[18] Thrasher, J. S.; Nielsen, J. B. *J. Fluorine Chem.* **1990**, *48*, 407.

product must arise from the following equilibria which exist among A–C:



$$\underset{\mathbf{A}}{2CF_3N{=}CF_2} \overset{F^-}{\rightleftharpoons} \underset{\mathbf{B}}{(CF_3)_2NCF{=}NCF_3} \underset{F^-}{\rightleftharpoons} \underset{\mathbf{C}}{(CF_3)_2NCF_2N{=}CF_2}$$

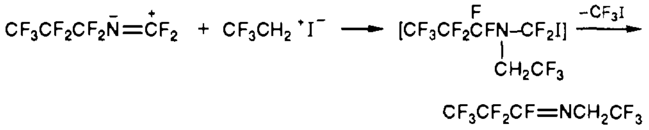
In these cases, only in the presence of strongly nucleophilic fluoride ion (not AgF) is the A → B equilibrium shifted markedly to the right, whereas F^- (AgF) is sufficiently active to isomerize C → B and finally to A. Thus, the most stable compound is $CF_3N{=}CF_2$, which leads to the sole isolable product.

Further attempts to synthesize additional tertiary amines from $(CF_3)_2NC(NMe_2){=}NCF_3$,[3] $SF_5N{=}C(C_2F_5)NMe_2$,[19] and $SF_5N{=}C(CF_3)C_2F_5$[17] failed. Only the starting materials were recovered.

An interesting result was the formation of a new polyfluoroazaalkene from the reaction of $C_3F_7N{=}CF_2$ with CF_3CH_2I, viz.

$$C_3F_7N{=}CF_2 + CF_3CH_2I \xrightarrow[100\ ^\circ C,\ 6\ d]{AgF,\ C_6H_5CN} \underset{\mathbf{19}}{C_2F_5CF{=}NCH_2CF_3}$$

No trace of the expected product, $C_3F_7N(CH_2CF_3)CF_3$, was found. A likely mechanism to rationalize this mode of behavior is



$$CF_3CF_2CF_2\overset{-}{N}{=}\overset{+}{C}F_2 + CF_3CH_2{}^{+}I^{-} \longrightarrow [CF_3CF_2\overset{F}{C}F\underset{CH_2CF_3}{N}{-}CF_2I] \xrightarrow{-CF_3I} CF_3CF_2CF{=}NCH_2CF_3$$

In the trap-to-trap separation of the reaction mixture, **19** was found in a trap at –65 °C and CF_3I was identified in the trap at –196 °C. This type of reaction in which the carbon–fluorine bond of the α-CF_2 group in C_3F_7 is broken with concomitant double-bond shift is rare. Work in this area is continuing.

Experimental Section

Materials. The reagents CF_3NCl_2, $C_2F_5NCl_2$, $C_3F_7NCl_2$, $CF_3N{=}CF_2$, $(CF_3)_2NN{=}CF_2$, $(CF_3)_2NN{=}CFN(CF_3)N(CF_3)_2$, and $SF_5N{=}C(Cl)C_2F_5$ were prepared according to literature methods.[1,2,6,18,20] Other chemicals were purchased as indicated and used as received: chlorine fluoride (Atochem North America); ClCN (Solkatronic Chemicals Inc.); CF_3CN, C_2F_5CN, $CF_2{=}CF_2$ and $CF_2{=}CFCl$ (PCR), $P(C_6H_5)_3$, CsCl;, AgF, CH_3CN, C_6H_5CN, CH_3I, C_2H_5I, CH_2I_2, $BrCH_2CH_2Br$, $Br_2CHCHBr_2$, and CF_3CH_2I (Aldrich Chemical Co., Inc.).

General Procedures. A conventional vacuum system, which consisted of a Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac thermocouple gauges, was used to handle gases and volatile liquids. Standard PVT techniques were used to quantitate starting materials and products. Fractional condensation (trap-to-trap distillation) and/or gas chromatography (HP5710A) were used for purification. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer with a 10-cm gas cell equipped with KBr windows. ^1H and ^{19}F NMR spectra were obtained with a Bruker AC 200 Fourier transform NMR spectrometer using $CDCl_3$ as solvent. Mass spectra were obtained with a VG 7070HS mass spectrometer by using chemical ionization techniques. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany, Photochemical reactions were conducted in a Rayonet ultraviolet reactor with 3000-Å lamps.

Preparation of $C_3F_7N(Cl)CF_2CFCl_2$ (1) and $C_3F_7N(Cl)CF_2CF_2Cl$ (2). Into a 75-mL stainless steel cylinder fitted with a Whitey valve was condensed 10 mmol of $C_3F_7NCl_2$ and 12 mmol of olefin ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) at –196 °C. After being warmed to room temperature, the cylinder was placed in a 65–70 °C oven for 12–14 h. The products were fractionated by trap-to-trap distillation.

Properties of $C_3F_7N(Cl)CF_2CFCl_2$ (1). This compound was isolated in a trap cooled to –25 °C having passed through a trap cooled to –10 °C. It was obtained in ~75% yield as a colorless liquid. Spectral data were as follows. IR (gas): 1349 w, 1274 s, 1218 vs, 1207 s, 1163 m, 1135 m, 1104 m, 1054 w, 1010 w, 940 m, 772 w, 733 s cm^{-1}. NMR ($CF_3^ACF_2^BCF_2^CNCF_2^DCF^ECl_2$): ^{19}F, δ –81.64 (A, mult, 3), –123.26 (B, mult, 2), –89.96 (C + D, mult, 4), –70.46 (E, mult, 1). MS CI [m/e (species), intensity]: 316/318 ($M^+ - ClF + 1$), 7.42/4.52; 296/298/300 ($M^+ - ClF_2$), 21.31/12.03/2.34; 214 ($C_4F_8N^+$), 24.07; 196/198 ($C_3F_4Cl_2N^+$), 4.30/1.95; 169 ($C_3F_7^+$), 8.67; 151/153 ($CF_2CFCl_2^+$), 8.18/5.03; 86/88 ($CF_2Cl^+ + 1$), 100.0/100. Anal. Calcd for $C_5F_{10}Cl_3N$: C, 16.26; F, 51.5; Cl, 28.7. Found: C, 16.21; F, 51.5; Cl, 28.54.

Properties of $C_3F_7N(Cl)CF_2CF_2Cl$ (2). This compound was found in the trap cooled to –25 °C, having passed through a trap at –10 °C. It was obtained in ~40% yield as a yellow liquid. Spectral data were as follows. IR (gas): 1350 m, 1284 s, 1249 vs, 1207 vs, 1185 vs, 1137 s, 1109 s, 1000 s, 975 m, 902 w, 879 w, 803 m, 786 m, 738 s cm^{-1}. NMR ($CF_3^ACF_2^BCF_2^CN(Cl)CF_2^DCF_2^ECl$): ^{19}F, δ –81.6 (A, t), –124.0 (B, t), –92.8 (C, tt), –91.4 (D, tq), –68.4 (E, t); $J_{C-D} = 18.8$ Hz, $J_{B-E} = 7.5$ Hz, $J_{C-E} = 7.5$ Hz, $J_{A-D} = 9.4$ Hz. MS CI [m/e (species), intensity]: 300/302 ($M^+ - ClF + 1$), 49.2/18.6; 280/282 ($M^+ - ClF_2$), 100.0/43.0; 264 ($M^+ - Cl_2F$), 39.1; 230/232 ($M^+ - CF_4Cl$), 6.2/1.9, 214 ($M^+ - CF_3Cl_2$), 29.2; 164 ($C_3F_6N^+$), 29.2; 135/137 ($C_2F_4Cl^+$), 55.9/18.4; 119 ($C_2F_5^+$), 56.0; 85/87 (CF_2Cl^+), 47.3/14.6. Anal. Calcd for $C_5F_{11}Cl_2N$: F, 59.21; Cl, 19.83; C, 17.00. Found: F, 57.1; Cl, 19.25; C, 17.01.

Preparation of $C_2F_5CF{=}NCF_2CFCl_2$ (3) and $C_2F_5CF{=}NCF_2CF_2Cl$ (4). By the stirring of 5 mmol of compound **1** or **2** with 10 mmol of $(C_6H_5)_3P$ at 25 °C for 4–6 h, compound **3** or **4** was formed. Also, when 5 mmol of compound **1** or **2** and 5 mmol of CsCl were stirred in CH_3CN for 5 d at 25 °C, compound **3** or **4** resulted.

Properties of $C_2F_5CF{=}NCF_2CFCl_2$ (3). This compound was found in the trap cooled to –78 °C, having passed through a trap at –40 °C. It was obtained in 77% yield as a colorless liquid. Spectral data were as follows. IR (gas): 1775 vs ($\nu_{C=N}$), 1344 m, 1320 s, 1274 m, 1223 vs, 1180 vs, 1128 s, 1104 s, 1018 s, 915 s, 863 w, 824 w, 766 w, 687 w, 481 w cm^{-1}. NMR ($CF_3^ACF_2^BCF^C{=}NCF_2^DCF^ECl_2$): ^{19}F, δ –83.3 (A, mult), –121.3 (B, d), –23.5 (C, mult), –92.7 (D, dd), –75.7 (E, mult); $J_{B-C} = 13.2$ Hz, $J_{C-D} = 18.8$ Hz, $J_{C-E} = 9.2$ Hz. MS CI [m/e (species), intensity]: 316/318/320 ($M^+ + 1$), 23.3/16.6/3.3; 296/298/300 ($M^+ - F$), 54.5/35.2/9.4; 262/264 ($M^+ - ClF + 1$), 9.3/3.9; 214 ($M^+ - CFCl_2$), 78.9; 151/153/155 ($C_2F_3Cl_2^+$), 24.9/15.5/8.8; 101 ($C_2F_4^+ + 1$), 53.2. Anal. Calcd for $C_5F_9Cl_2N$: C, 19.05; F, 54.29; Cl, 22.22. Found: C, 18.81; F, 52.2; Cl, 22.80.

Properties of $C_2F_5CF{=}NCF_2CF_2Cl$ (4). This compound was found with another azaalkene in the trap cooled to –85 °C, having passed through a trap at –70 °C. After purification by using a 4-ft. Kel-F on Haloport F column, it was obtained in ~40% yield as a yellow liquid. Spectral data were as follows. IR (gas): 1779 s ($\nu_{C=N}$), 1350 m, 1317 m, 1239 vs, 1209 vs, 1190 s, 1130 s, 1114 s, 1024 m, 966 m, 946 w, 481 w cm^{-1}. NMR ($CF_3^ACF_2^BCF^C{=}NCF_2^DCF_2^ECl$): ^{19}F, δ –83.3 (A, mult), –121.3 (B, d), –22.8 (C, mult), –95.5 (D, dt), –73.6 (E, mult); $J_{C-D} = 18.8$ Hz, $J_{D-E} = 3.77$ Hz, $J_{B-C} = 13.2$ Hz. MS CI [m/e (species), intensity]: 300/302 ($M^+ + 1$), 14.5/4.0; 280/282 ($M^+ - F$), 36.5/10.5; 264 ($M^+ - Cl$), 8.8; 230 ($M^+ - CF_3$), 1.8; 214 ($M^+ - CF_2Cl$), 32.4; 135/137 ($C_2F_4Cl^+$), 17.13/5.1; 119 ($C_2F_5^+$), 43.5; 100 ($C_2F_4^+$), 21.3; 85/87 (CF_2Cl^+), 23.2/6.9.

Preparation and Characterization of $C_3F_7N(N{=}CCl_2)CF_2CFCl_2$ (5). A 5-mmol amount of **1** and 30–35 mmol of ClCN were condensed at –196 °C into a 2-L quartz vessel fitted with a Kontes Teflon stopcock. After the vessel warmed to 25 °C, it was exposed to UV radiation (3000 Å) for 6–7 h. The compound remained in the quartz vessel at 25 °C under dynamic vacuum in ~10% yield, with the volatile compound $C_3F_7N{=}CF_2$ (~90%) obtained as byproduct. Spectral data were as follows. IR (gas): 1651 vs ($\nu_{C=N}$), 1572 m, 1505 m, 1476 m, 1409 w, 1343 m, 1278 s, 1235 s, 1203 s, 1127 s, 1039 s, 1018 s, 939 s, 908 s, 846 m, 825 m, 783 m, 738 m, 681 w cm^{-1}. NMR ($CF_3^ACF_2^BCF_2^CN(N{=}CCl_2)CF_2^DCF^ECl_2$): ^{19}F, δ –81.4 (A, mult), –123.7 (B, t), –95.6 (C, mult), –91.8 (D, t), –72.3 (E, q); $J_{A-E} = 7.3$ Hz, $J_{B-C} = 17.9$ Hz, $J_{C-D} = 10.2$ Hz. MS CI [m/e (species), intensity]: 430 (M^+), 0.7; 411/413 ($M^+ - F$), 2.0/1.3; 395/397 ($M^+ - Cl$), 2.6/2.0; 329/331 ($M^+ - CFCl_2$), 11.7/6.8; 296/298 ($M^+ - CCl_2FN$), 2.2/1.6; 214 ($C_4F_8N^+$), 5.8; 169 ($CF_3CF_2CF_2^+$), 7.8; 135/137 (FCF_2CFCl^+), 9.8/2.8; 101/103 ($CFCl_2^+$), 76.0/50.6.

Preparation and Characterization of $C_3F_7N(Cl)CF_3$ (6). A 5-mmol amount of $C_3F_7N{=}CF_2$ and 5.5 mmol of ClF were condensed into a stainless steel vessel at –196 °C, warmed to 25 °C, and held for 10–12 h. A colorless liquid in ~100% yield was found in a trap cooled to –60 °C, having passed through a trap at –40 °C. Spectral data were as follows. IR (gas): 1350 s, 1257 vs, 1132 vs, 1085 w, 1016 s, 1000 vs, 953 w, 873 m, 845 s, 755 m, 734 s, 716 s, 646 w, 538 w cm^{-1}. NMR ($CF_3^ACF_2^BCF_2^CN(Cl)CF_3^D$): ^{19}F, δ –81.7 (A, mult), –125.1 (B, mult),

---

(19) Patel, N. To be published (University of Idaho).
(20) Krumm, B.; Kirchmeier, R. L.; Shreeve, J. M. To be published.

–96.0 (C, mult), –60.1 (D, mult). MS CI [*m/e* (species), intensity]: 234 ($M^+ - ClF + 1$), 100.0; 214 ($M^+ - ClF_2$), 100.0; 164 ($M^+ - C_3F_6N$), 69.5; 146 ($C_3F_5N^+ + 1$), 22.3; 114 ($C_2F_4N^+$), 100.0; 101 ($C_2F_4^+ + 1$), 51.6; 95 ($C_2F_3N^+$), 29.6; 84 ($CF_3N^+ + 1$), 39.6. Anal. Calcd for $C_4F_{10}ClN$: C, 16.72; F, 66.20; Cl, 12.20. Found: C, 16.64; F, 65.8; Cl, 12.48.

Reactions of Azaalkenes with CH_3I, C_2H_5I, or C_6H_5I. Preparation of $R_fN(R)CF_3$ ($R = CH_3, C_2H_5, C_6H_5$). A 6-mmol amount of AgF and ~4 mL of C_6H_5CN were added to a 100-mL flask equipped with a Kontes Teflon stopcock. The flask was evacuated at –196 °C, and 5 mmol of azaalkene and 6 mmol of alkyl or aryl iodide were condensed into the flask, which was warmed to 25 °C and stirred in the dark for 3 d. The products were separated by trap-to-trap distillation.

Properties of $(CF_3)_2NCH_3$ (7). This compound was found in 75% yield in a trap at –110 °C trap, having passed through a trap at –78 °C. It was identified by comparing the infrared and NMR data obtained with the data reported in the literature.[11,12]

Properties of $(CF_3)_2NC_2H_5$ (8). This compound was found in 70% yield in a trap at –115 °C, having passed through a trap at –78 °C. When CsF was used in place of AgF, slightly better yields were obtained. It was identified by comparing the infrared and NMR data obtained with the data reported in the literature.[12] Compound **8** boils at 30 °C (ΔH_v = 6.5 kcal/mol; ΔS = 21.5 eu).

Properties of $C_2F_5N(CF_3)CH_3$ (9). This compound was found in the trap cooled to –100 °C, having passed through a trap at –78 °C. The yield of the compound was ~67%. Spectral data were as follows. IR (gas): 2980 w, 2877 w, 1484 m, 1460 m, 1328 vs, 1229 vs, 1192 s, 1149 vs, 1094 s, 932 w, 886 s, 717 s, 660 w, 628 w cm^{-1}. NMR ($CF_3^{A}CF_2^{B}N(CF_3^{C})CH_3^{D}$): ^{19}F, δ –84.5 (A, qq), –99.7 (B, qq), –57.8 (C, tq); ^1H, δ 2.8 (D, mult); $J_{A-C} = 3.5$ Hz, $J_{C-D} = 1.8$ Hz, $J_{B-D} = 1.9$ Hz, $J_{A-D} = 1.9$ Hz, $J_{B-C} = 13.2$ Hz. MS CI [*m/e* (species), intensity]: 216 ($M^+ - H$), 6.5; 198 ($M^+ - F$), 100; 148 ($M^+ - CF_3$), 100; 128 ($M^+ - CF_4H$), 10.5; 119 ($C_2F_5^+$), 28.2; 110 ($M^+ - CF_5$), 17.5; 101 ($C_2F_4^+ + 1$), 17.6; 96 ($C_2F_3N^+ + 1$), 12.4. Anal. Calcd for $C_4F_8H_3N$: C, 22.12; N, 6.45; H, 1.38. Found: C, 21.99; N, 6.42; H, 1.43.

Properties of $C_2F_5N(CF_3)C_2H_5$ (10). The compound was found in 40% yield in the trap cooled to –100 °C, having passed through a trap at –78 °C. It is a colorless liquid. Spectral data were as follows. IR (gas): 2997 w, 1403 w, 1351 m, 1322 s, 1262 vs, 1223 vs, 1185 w, 1148 s, 1132 m, 1084 vs, 896 w cm^{-1}. NMR ($CF_3^{A}CF_2^{B}N(CF_3^{C})CH_2^{D}$-$CH_3^{E}$): ^{19}F, δ –84.9 (A, q), –98.3 (B, qt), –54.5 (C, mult); ^1H, δ 3.28 (D, qt), 1.23 (E, tq); $J_{A-E} = 4.7$ Hz, $J_{B-C} = 12.9$ Hz, $J_{B-D} = 2.1$ Hz, J_{D-E} = 7.1 Hz. MS CI [*m/e* (species), intensity]: 230 ($M^+ - H$), 4.6; 216 ($M^+ - CH_3$), 100; 198 ($M^+ - CH_3F + 1$), 7.1; 184 ($M^+ - C_2H_5F + 1$), 100; 162 ($M^+ - CF_3$), 45.5; 134 ($M^+ - C_2H_5 - CF_3 + 1$), 12.5; 128 ($C_3F_4H_2N^+$), 43.6; 119 ($C_2F_5^+$), 31.9; 114 ($C_2F_4N^+$), 15.5; 103 ($NC_4F_2H_3^+$), 100; 100 ($C_2F_4^+$), 100; 89 ($NC_3F_2H^+$), 59.0.

Properties of $C_3F_7N(CF_3)CH_3$ (11). This compound (60% yield) was found in a trap cooled to –78 °C, having passed through a trap at –60 °C. It is a colorless liquid. Spectral data were as follows. IR (gas): 2981 w, 1485 m, 1459 m, 1340 vs, 1278 s, 1219 vs, 1139 vs, 1099 vs, 1029 m, 987 vs, 852 s, 758 m, 725 w, 535 w, 482 w cm^{-1}. NMR ($CF_3^{A}CF_2^{B}CF_2^{C}N(CF_3^{D})CH_3^{E}$): ^{19}F, δ –81.9 (A, t), –127.4 (B, q), –96.1 (C, mult), –57.7 (D, tt); ^1H, δ 2.87 (E, mult); $J_{A-C} = 9.8$ Hz, $J_{B-D} = 5.6$ Hz, $J_{C-D} = 15.0$ Hz. MS CI [*m/e* (species), intensity]: 268 ($M^+ + 1$), 2.2; 248 ($M^+ - F$), 100.0; 226 ($M^+ - H_3F_2$), 4.5; 214 ($M^+ - CH_3F_2$), 1.3; 198 ($M^+ - CF_3$), 2.0; 178 ($M^+ - CF_4H$), 1.0; 169 ($C_3F_7^+$), 6.2; 160 ($C_4F_5H_3N^+$), 4.6; 148 ($M^+ - C_2F_5$), 56.2; 131 ($C_3F_5^+$), 0.5; 119 ($C_2F_5^+$), 4.2; 114 ($C_2F_4N^+$), 3.5; 100 ($CF_2CF_2^+$), 3.0; 96 ($CHNCF_3^+$), 3.1.

Properties of $(CF_3)_2NC_6H_5$ (12). This product was isolated in 50% yield in a trap at –78 °C, having passed through a trap at –40 °C. It was identified by comparison of infrared and NMR data with the spectra reported in the literature.[3]

Properties of $(CF_3)_2NSi(CH_3)_3$ (13) and $(CF_3)_2NSCF_3$ (14). Compounds of **13** and **14** were prepared by mixing $(CH_3)_3SiCl$ and CF_3SCl, respectively, with CsF, $CF_3N{=}CF_2$, and CH_3CN. The products were separated by trap-to-trap distillation, and **13** and **14** were identified by comparing the infrared and NMR spectra obtained with the literature data.[14,15]

Properties of $(CF_3)_2NN(CH_3)CF_2N(CF_3)N(CF_3)_2$ (15). This compound was found in a trap held at –90 °C (~55% yield), having passed a trap at –78 °C. Spectral data were as follows. IR (gas): 2980 m, 2960 w, 1848 m, 1726 w, 1658 w, 1348 m, 1289 s, 1240 s, 1213 s, 1180 vs, 1118 vs, 1043 s, 981 m, 909 s, 848 m, 817 s, 796 m, 654 w, 524 w, 481 w cm^{-1}. NMR [$(CF_3)_2^{A}NN(CH_3)^{B}CF_2^{C}N(CF_3)^{D}N(CF_3)_2^{E}$]: ^{19}F, δ –72.0 (A, mult), –67.;8 (D, E, mult), –60.6 (C, mult); ^1H, δ 3.01 (B, mult). MS CI [*m/e* (species), intensity]: 466 (M^+), 2.5; 447 ($M^+ - F$), 9.8; 432 ($M^+ - CH_3F$), 5.6; 398 ($M^+ - CF_3 + 1$), 15.6; 378 ($M^+ - CF_4$), 4.8; 326 ($M^+ - C_2F_6H_2$), 1.6; 314 ($M^+ - N(CF_3)_2$), 2.0; 246 ($C_4F_8N_3H_4^+$), 11.5; 230 ($C_3F_8N_3^+$), 24.1; 198 ($C_3F_7N_2H^+$), 12.8; 178 ($C_3F_6N_2^+$), 1.1; 153 ($C_2F_6NH^+$), 41.1; 152 ($C_2F_6N^+$), 48.9; 133 ($C_2F_5N^+$), 2.5; 83 (CF_3N^+), 31.2; 69 (CF_3^+), 100.

Properties of $SF_5N(CH_3)C_3H_7$ (16). Compound **16** was found in a trap at –78 °C (60% yield), having passed through a –35 °C trap. Spectral data were as follows. IR (gas): 2967 m, 1541 w, 1515 m, 1481 w, 1341 m, 1235 vs, 1205 s, 1146 s, 1096 w, 1016 s, 980 s, 914 s, 868 m, 832 w, 790 w, 751 s, 700 m, 607 m cm^{-1}. NMR [$SF_4^{A}F^{B}N(CH_3)^{C}CF_2^{D}CF_2^{E}$-$CF_3^{F}$]: ^{19}F, δ 69.1 (A, d), 76.9 (B, p), –91 (D, mult), –120 (E, mult), –81.7 (F, mult); J_{SF-SF_4} = 145 Hz; ^1H, δ 3.09 (C, m). MS CI [*m/e* (species), intensity]: 326 ($M^+ + 1$), 1.5; 325 (M^+), 15.2; 272 ($M^+ - CH_3F_2$), 1.0; 243 ($M^+ + 2 - C_2F_3H_3$), 7.2; 225 ($M^+ - C_2F_4$), 10.6; 211 ($M^+ + 1 - C_3F_4H_3$), 3.0; 206 ($M^+ - C_2F_5$), 17.7; 198 ($M^+ - SF_5$), 1.0; 183 ($M^+ - CH_3 - SF_5$), 1.5; 169 ($C_3F_7^+$), 5.9; 160 ($C_3F_4H_2NS^+$), 11.0; 154 ($SF_5NC^+ + 1$), 2.5; 142 ($SF_5N^+ + 1$), 2.9; 129 ($C_3F_4NH_2^+$), 2.1; 127 (SF_5^+), 45.3; 119 ($C_2F_5^+$), 76.8; 114 ($C_2F_4N^+$), 2.9; 100 ($C_2F_4^+$), 15.5; 89 (SF_3^+), 7.7; 79 ($C_2F_2NH_3^+$), 3.7; 69 (CF_3^+), 100. Anal. Calcd for $C_4F_{12}H_3NS$: C, 14.7; F, 70.2. Found: C, 13.9; F, 69.8.

Preparation of $(CF_3)_2NCH_2CH_2N(CF_3)_2$ (17) and $[(CF_3)_2N]CHCH$-$[N(CF_3)_2]_2$ (18). To a 500-mL round-bottomed flask equipped with a Teflon stopcock was added 7 mmol of silver fluoride. The flask was cooled to –196 °C and evacuated, and 6 mmol of acetonitrile was added. The mixture was stirred at 25 °C for 1 h, after which 6 mmol of $CF_3N{=}CF_2$ was added and stirring was continued for 3 h. To this mixture was added 3 mmol of $BrCH_2CH_2Br$ or 1.5 mmol of $Br_2CHCHBr_2$. After 12 h at 25 °C, the products were separated by low-temperature trap-to-trap distillation.

Properties of $(CF_3)_2NCH_2CH_2N(CF_3)_2$ (17). Compound **17** was found in 60% yield in a trap at –70 °C, having passed through a trap at –30 °C. Spectral data were as follows. IR (gas) 2967 m, 2945 w, 1377 w, 1286 w, 1211 s, 1187 s, 1118 s, 1084 vs, 1029 s, 910 s, 846 vs, 817 s, 735 m, 603 m, 481 m cm^{-1}. NMR [$(CF_3)_2^{A}NCH_2^{B}CH_2N(CF_3)_2$]: ^{19}F, δ –56.7 (A, s); ^1H, δ 3.43 (B, s). MS CI [*m/e* (species), intensity]: 332 (M^+), 1.1; 264 ($M^+ + 1 - CF_3$), 1.0; 244 ($M^+ - CF_4$), 1.5; 223 ($M^+ - CF_5H_2$), 1.8; 203 ($M^+ - CF_6H_3$), 2.0; 195 ($M^+ + 1 - C_2F_6$), 1.9; 181 ($M^+ + 1 - N(CF_3)_2$), 2.5; 149 ($C_5F_3N_2H_4^+$), 27.4; 109 ($C_3F_3NH_2^+$), 10.4; 107 ($C_3F_3N^+$), 13.2; 97 ($CF_3NCH_2^+$), 15.0; 95 (CF_3NC^+), 19.8; 83 (CF_3N^+), 23.5; 69 (CF^+), 100. Compound **18** boils at 109.9 °C (ΔH_v = 10.0 kcal/mol; ΔS = 26.3 eu).

Properties of $[(CF_3)_2N]_2CHCH[N(CF_3)_2]_2$ (18). Compound **18** was isolated in low yield in a trap at –50 °C, having passed through a trap at –25 °C. Spectral data were as follows. IR (gas): 2969 m, 2941 m, 1408 w, 1213 s, 1180 s, 1118 s, 1084 vs, 1043 s, 910 s, 846 vs, 817 s, 735 m, 723 w, 481 w cm^{-1}. NMR [$\{(CF_3)_2^{A}N\}_2CH^{B}]_2$: ^{19}F, δ –68.0 (A, s); ^1H, δ 5.65 (B, b). MS CI [*m/e* (species), intensity]: 526 ($M^+ - CF_3$-HF-F), 0.4; 381 ($M^+ - (CF_3)_2N - C_2F_4H$), 1.0; 344 ($[(CF_3)_2N]_2$-$CHCHN^+$), 2.0; 334 ($C_8F_{11}N_2H^+$), 3.9; 299 ($C_5F_{11}N_2H_2^+$), 16.0; 266 ($C_6F_8N_3^+$), 22.2; 264 ($C_7F_8N_2^+$), 26.2; 219 ($C_5F_6N_3H_3^+$), 1.6; 206 ($C_4F_6N_3H_2^+$), 15.9; 204 ($C_5F_6N_2H_2^+$), 40.3; 185 ($C_5F_5N_2H_2^+$), 43.9; 153 ($C_2F_6NH^+$), 37.8; 103 ($C_3F_2N_2H^+$), 79.5; 101 ($C_2F_4H^+$), 100; 69 ($CF_3^+$), 24.7.

Preparation and Properties of $CF_3CF_2CF{=}NCH_2CF_3$ (19). A 6-mmol amount of AgF and ~4 mL of C_6H_5CN were added to a 100-mL flask equipped with a Kontes Teflon stopcock. After evacuation of the flask at –196 °C, 5 mmol of $CF_3CF_2CF_2N{=}CF_2$ and 6 mmol of CF_3CH_2I were condensed into the flask. The mixture was warmed and stirred in the dark at 100 °C for 6 d. The mixture was separated by trap-to-trap distillation, and **19** was found in the trap cooled to –65 °C, having passed through a trap at –50 °C. Spectral data were as follows. IR (gas): 2989 w, 1811 vs ($\nu_{C=N}$), 1416 m, 1352 m, 1317 vs, 1280 vs, 1233 vs, 1190 vs, 1153 vs, 1128 m, 1053 vs, 977 m, 737 s, 665 w cm^{-1}. NMR ($CF_3^{A}CF_2^{B}CF^{C}{=}NCH_2^{D}CF_3^{E}$): ^{19}F, δ –83.4 (A, t), –121.9 (B, q), –77.6 (C, mult), –74.3 (E, t); ^1H, δ 4.66 (D, q); $J_{A-B} = 1.8$ Hz, $J_{D-E} = 7.5$ Hz. MS CI [*m/e* (species), intensity]: 247 (M^+), 41.7; 227 ($M^+ - HF$), 100; 210 ($M^+ - 2F + 1$), 18.7; 191 ($M^+ - 3F + 1$), 17.5; 179 ($M^+ - CF_3 + 1$), 6.7; 165 ($M^+ - CF_3CH_2 + 1$), 1.2; 147 ($M^+ - CF_3 - CF$), 26.1; 127 ($M^+ - CF_3 - CF_2 - H$), 37.0; 119 ($C_2F_5^+$), 98.1; 100 (CF_3CF^+), 8.0; 83 ($CF_3CH_2^+$), 100.

Acknowledgment. We are grateful for the support of the National Science Foundation (Grant CHE-9003509), the Air Force Office of Scientific Research (Grant 91-0189), and Daikin Industries, Ltd.