reference is cited in the table. Data for new compounds and new data for known compounds are given below and in Table II.

Reaction of $(CF_3)_2C{=}NH$ with $S_2O_6F_2$. The relative amounts of the products $[(CF_3)_2C{=}N]_2$, $(CF_3)_2C{=}NOSO_2F$, and $(CF_3)_2C(OSO_2F)N{=}N(OSO_2F)C(CF_3)_2$ varied randomly from reaction to reaction. They were purified using gas chromatography and the latter two compounds were characterized.

$(CF_3)_2C{=}NOSO_2F$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The equation $\log P_{\mathrm{mm}} = 9.22 - 2180/T$ describes the vapor pressure curve over the temperature range from 309 to 339°K from which ΔH_v (9.9 kcal/mol), ΔS_v (28.8 eu), and the boiling point (71°) are obtained.

Anal. Calcd: N, 5.32; S, 12.17; F, 50.6; C, 13.69. Found: N, 5.29; S, 12.37; F, 50.6; C, 13.79.

The compound was also prepared in 94% yield by the reaction of 1.3 mmol of $BrOSO_2F$ with 1.5 mmol of $(CF_3)_2C{=}NCl$ at 0° for 6 hr. The reactants were combined at liquid oxygen temperature and allowed to warm slowly to 0°. The products were separated by a trap-to-trap distillation.

$(CF_3)_2C(OSO_2F)N{=}N(OSO_2F)C(CF_3)_2$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The equation $\log P_{\mathrm{mm}} = 7.127 - 1850/T$ describes the vapor pressure curve over the temperature range from 342 to 387°K. The compound decomposes in glass at 113° to give SiF_4, $[(CF_3)_2C{=}N]_2$, and others.

Anal. Calcd: C, 13.69; F, 50.6; N, 5.32; S, 12.17. Found: C, 13.75; F, 50.5; N, 5.46; S, 12.13.

The compound was prepared previously in greater than 95% yield by the reaction of $S_2O_6F_2$ with $[(CF_3)_2C{=}N]_2$ at 25° for 2 hr.[19]

Reaction of CH_2Cl_2 with $S_2O_6F_2$. When a mixture of CH_2Cl_2 (1 mmol), diluted 4:1 with Freon 11, and $S_2O_6F_2$ (1 mmol) was held at −25° for 2 hr, $HCCl_2OSO_2F$ (60%), HSO_3F, $COCl_2$, and $S_2O_5F_2$ formed. Decomposition products obtained in the reaction between $HCCl_2OSO_2F$ and $S_2O_6F_2$ are listed in Table I.

$HCCl_2OSO_2F$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The vapor pressure curve was linear to 87°. Incomplete decomposition in glass of the compound occurred at 25° over a period of 24 hr to give SO_2, SiF_4, and a brown, involatile residue.

Reaction of NH_3 with $S_2O_6F_2$. NH_3 was allowed to react with $S_2O_6F_2$ in a 1:3 molar ratio. In the gas phase at 0°, the reaction yielded a white solid, and excess $S_2O_6F_2$ (62%). The solid was extracted with methanol. Part of the solid was soluble and, upon evaporation of the methanol, was determined to be NH_4OSO_2F by comparison with the infrared spectrum of an authentic sample. The insoluble portion decomposed at 280° and was insoluble in CCl_3F, $(CH_3)_4Si$, CH_2Cl_2, CCl_4, PhCl, $(CF_3)_2CO$, CH_3CN, $(CH_3)_2CO$, C_2H_5OH, $HC(O)N(CH_3)_2$, NH_3(aq), $(CH_3)_2O$, and $(CH_3)_2SO$. It was decomposed by H_2O. Elemental analysis suggests a compound of empirical formula $(NH_3)_5S_3O_9F_2$. The infrared spectrum of the insoluble white solid contained bands at 3120 (s, b), 1410 (s), 1375 (sh), 1260 (s), 1195 (s), 1087 (w), 1023 (m), 863 (m), and 580 (b) cm^{-1}.

Reaction of Toluene with $S_2O_6F_2$. Toluene diluted 4:1 with CCl_3F was allowed to react with $S_2O_6F_2$ in a 1:1 ratio at −63°. The gaseous peroxide was added in small aliquots. Reaction was extremely vigorous and always accompanied by charring. Yields were very low and the fluorosulfate product was not separated from the other involatile products. Volatile materials which resulted from the reaction were identified as excess toluene, CCl_3F, $S_2O_5F_2$, SiF_4, and SO_2.

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Registry No. $S_2O_6F_2$, 13709-32-5; HCl, 7647-01-0; CF_3H, 75-46-7; CF_3SH, 1493-15-8; CF_3SSCF_3, 372-64-5; CF_3CF_2H, 354-33-6; CF_3CH_2OH, 75-89-8; $CF_3C(O)SH$, 2925-25-9; $[CF_3C(O)S]_2$, 21690-87-9; NH_3, 7664-41-7; $C_2F_5C(CF_3)_2OH$, 6188-98-3; $(CF_3)_3COH$, 2378-02-1; $HCFCl_2$, 75-43-4; $(CF_3)_2NOH$, 359-63-7; $(CF_3)_2NH$, 371-77-7; H_2S, 7783-06-4; $(CF_3)_2C{=}NH$, 1645-75-6; $[(CF_3)_2C{=}N]_2$, 1619-84-7; $HCCl_2OSO_2F$, 42016-50-2; CH_2Cl_2, 75-09-2; CH_3Br, 74-83-9; CH_3OSO_2F, 421-20-5; CH_3CH_2OH, 64-17-5; OCH_3, 108-88-3; $(CF_3)_2NOSO_2F$, 21950-99-2; $(CF_3)_2C{=}NSO_3F$, 42016-51-3; $((CF_3)_2C(OSO_2F)N)_2$, 42030-68-2; $CH_2(OSO_2F)_2$, 42016-52-4; $BrOSO_2F$, 13997-93-8; $(CF_3)_2C{=}NCl$, 10181-78-9; $(NH_3)_5S_3O_9F_2$, 39405-86-2; CF_3CO_2H, 76-05-1.

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[19] R. F. Swindell, University of Idaho, unpublished results.

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Polar Additions of Chlorine Monofluoride and Chlorine Fluorosulfate to Fluorinated Isocyanates

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The addition reactions of chlorine monofluoride and chlorine fluorosulfate with various fluorinated isocyanates give a new class of compounds, $R_fN(Cl)C(O)R_f'$. The new chloramines $CF_3N(Cl)C(O)F$, $CF_3C(O)N(Cl)C(O)F$, $FC(O)N(Cl)C(O)F$, $CF_3N(Cl)C(O)OSO_2F$, $CF_3C(O)N(Cl)C(O)OSO_2F$, and $FC(O)N(Cl)C(O)OSO_2F$, as well as the new secondary amines $CF_3C(O)N(H)C(O)F$ and $FC(O)N(H)C(O)F$, have been synthesized and characterized. The previously known compounds $Cl_2NC(O)F$ and $CF_3N(H)C(O)F$ were also prepared.

Chlorine monofluoride is a very versatile reagent which provides a route to the controlled fluorination and/or chlorofluorination of a variety of systems. With fluorinated compounds which contain the -N=S= linkage, *e.g.*, $R_fN{=}S{=}O$[2] and $R_fN{=}SF_2$,[3] 2 mol of ClF adds with concomitant severing of the nitrogen-sulfur double bond to form dichloramines, $-NCl_2$, and the respective sulfur(IV)-fluoro compounds. Compounds that result from complete saturation of the carbon-nitrogen multiple bonds in nitriles[4,5] and imines[4,6,7] by ClF are the sole products. Neither carbon-nitrogen bond breaking nor partial saturation of a triple bond is observed. Pursuing our study of the chemistry of ClF and isocyanates,

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Table I. Reaction Conditions

Reactants (mmol)	Conditions	Trapping temp,[a] °C	Product(s) (yield, %)
CF_3NCO (3.6), ClF (6.2)	−78°, 0.5 hr[b] 25°, 1 hr	−78, −56	$CF_3N(Cl)C(O)F$ (78%), ClF, COF_2, CO_2, CF_3NCO, Cl_2
$CF_3C(O)NCO$ (9.7), ClF (19.4)	25°, 12 hr[b]	−45, −23	$CF_3C(O)N(Cl)C(O)F$ (75%), ClF, Cl_2, COF_2, CO_2, CF_3Cl, $CF_3C(O)NCO$
$FC(O)NCO$ (35.0), ClF (83.0)	25°, 12 hr[c]	−56, −40	$(FC(O))_2NCl$ (89%), ClF, Cl_2; COF_2, $FC(O)NCO$
$ClNCO$ (1.1), ClF (1.4), KF (5.0)	−78°, 0.5 hr[b] 25°, 1 hr		$Cl_2NC(O)F$[3] (estd 40%) + others from $HNCO$ impurities in the $ClNCO$
CF_3NCO (36.6), $ClOSO_2F$ (24.4)	−78°, 0.5 hr[d] 25°, 0.5-hr shaking	−40, −30	$CF_3N(Cl)CO_2SO_2F$ (96%), CF_3NCO, Cl_2, $S_2O_5F_2$, $CF_3N(Cl)C(O)F$
$CF_3C(O)NCO$ (3.5), $ClOSO_2F$ (3.2)	25°, 12 hr[d]	−20, +25	$CF_3C(O)N(Cl)CO_2SO_2F$ (estd 90–95%), $S_2O_5F_2$, $CF_3C(O)N(Cl)C(O)F$, $CF_3C(O)NCO$
$FC(O)NCO$ (6.0), $ClOSO_2F$ (5.4)	25°, 1 day[d]	−30, −20	$FC(O)N(Cl)CO_2SO_2F$ (estd 90–95%), $S_2O_5F_2$, Cl_2, $FC(O)NCO$
$CF_3N(Cl)C(O)F$ (1.7), HCl (3.8)	−78°, 0.5 hr[d]	−40, −20	$CF_3N(H)C(O)F$ (65%), Cl_2 (100%), CF_3NCO, HCl, solids
$CF_3C(O)N(Cl)C(O)F$ (3.5), HCl (4.2)	25°, 0.25 hr[d]	−20, +25	$CF_3C(O)N(H)C(O)F$ (estd 60–70%), Cl_2 (100%), $CF_3C(O)NCO$, HCl, solids
$FC(O)N(Cl)C(O)F$ (4.0), HCl (4.3)	25°, 0.25 hr[d]	−30, −20	$(FC(O))_2NH$ (estd 60–70%), Cl_2 (100%), $FC(O)NCO$, HCl, solids

[a] Temperature at which compound traps, lowest temperature trap that compound passes. [b] 30-ml stainless steel vessel. [c] 75-ml stainless steel vessel. [d] 90-ml Pyrex glass vessel with Teflon stopcock.

we now report the successful 1:1 addition of ClF and $ClOSO_2F$ to perfluorinated isocyanates with essentially no C-N bond breakage.

Based on the number of recent reviews,[8-10] reactions which involve the isocyanate group continue to be an area of considerable interest. Normally four-membered heterocycles result when unsaturated compounds, such as sulfoxides, olefins, enamines, acetylenes, carbonyls, and ketenes, add to isocyanates. Dipolar additions occur readily with compounds that contain acid hydrogens (C-H, N-H, S-H, O-H, P-H), as well as with hydrogen halides and hydrogen pseudohalides. Studies of additions of a polar interhalogen and a halogen pseudohalide to fluorinated isocyanates were undertaken: $R_fNCO + ClX \rightarrow R_fN(Cl)C(O)X$ ($X = F, OSO_2F$; $R_f = CF_3, CF_3C(O), FC(O), Cl$).

The chloramines which result from reaction with ClF react readily with hydrogen chloride to eliminate chlorine and to form new substituted fluoramines. Decomposition occurs with the fluorosulfate derivatives.

Experimental Section

General Methods. A standard Pyrex high-vacuum system equipped with a Heise Bourdon tube gauge was used in all reactions. Purification of starting materials and products was accomplished by fractional condensation. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrometer using a 10-cm gas cell fitted with sodium chloride or silver chloride disks depending on the corrosiveness of the sample. Liquid infrared spectra of the slightly volatile compounds were recorded by placing a thin film between silver chloride disks. ^{19}F nmr spectra were obtained on a Varian HA-100 spectrometer at 94.1 MHz with trichlorofluoromethane as an internal reference. ^1H nmr spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as an internal reference. A Hitachi Perkin-Elmer RMU-6E spectrometer operated at an ionization potential of either 70 or 17 eV was used to obtain mass spectra. Vapor pressure measurements and molecular weight determinations were obtained by the methods of Kellogg and Cady[11] and Regnault, respectively. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Gottingen, West Germany. Unstable compounds were fused with excess sodium metal and fluorine content determined with a fluoride ion electrode.

Materials. NaN_3 and $KNCO$ (Baker) and ClF (Ozark-Mahoning) were used as received. $CF_3C(O)Cl$ (PCR and Columbia Organic) was carefully purified by fractional condensation. Published methods were used for the preparation of $ClOSO_2F$,[12] $ClNCO$,[13] and $AgNCO$.[14] CF_3NCO was prepared by a modification of the literature method.[15] Carefully purified $CF_3C(O)Cl$ (10 mmol) reacted with excess NaN_3 (15 mmol) (*caution*) in a 75-ml stainless steel vessel without solvent. The resulting $CF_3C(O)N_3$ was purified by fractional condensation and a Curtius rearrangement effected by heating the latter for 3 hr at 120° in the presence of chloroform solvent. Good yields of CF_3NCO, which may be contaminated with up to 25% $CF_3N{=}CF_2$, resulted. *Caution! $CF_3C(O)N_3$ detonates upon mechanical and thermal shock. Shields are an absolute necessity at all times.* We have found that commercially available $CF_3C(O)Cl$ may contain up to 85% HCl as well as other slightly volatile hydrogen-containing materials. Purity of the $CF_3C(O)Cl$ should be checked by high-pressure infrared and molecular weight every time the preparation is attempted to eliminate any possibility of hydrazoic acid formation. Metal reactors designed for high-pressure reactions should always be used and reactant quantities must never exceed 10 mmol. A method which is an apparently much safer and more convenient preparation of CF_3NCO has been reported recently. $COCl_2$, KF, and $BrCN$, when heated at 45-50° in an acetonitrile solvent, yielded COF_2 and CF_3NCO.[16] $CF_3C(O)NCO$ or $FC(O)NCO$ was prepared by the reaction of $CF_3C(O)Cl$ (80 mmol) or $FC(O)Cl$ (80 mmol) with $AgNCO$ (150 mmol) in a metal vessel at 120° for 12 hr. Some polymerization resulted if the reactions were allowed to cool before removal of the isocyanate. If the reaction time was increased, excessive amounts of CO_2 resulted.

General Reaction Procedure for ClF and $ClOSO_2F$ Addition Reactions. The two reactants were condensed in an appropriate vessel at −195° and the mixture was allowed to warm to the reaction temperature (Table I). Fractional condensation was used to separate the addition compounds from the reaction products. Sometimes the trapping procedure was repeated several times to ensure purity of the chloramine. Both $CF_3C(O)N(Cl)CO_2SO_2F$ and $FC(O)N(Cl)CO_2SO_2F$ are slightly volatile liquids which can only be transferred at less than 10^{-3} Torr under a dynamic vacuum. Further transfers of these materials were carried out by using a syringe in a drybox. The products formed are independent of the mole ratio of the reactants. Normally the reactant ratios were adjusted to facilitate purification

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Table II. Elemental Analysis and Thermodynamic Data

	%							ΔH_v,		log $P_{Torr} = A - B/T$	
Compd	C	F	N	Cl	S	Mol wt	Bp, °C	kcal/mol	ΔS_v, eu	A	B
$CF_3N(Cl)C(O)F$	14.58 (14.50)[a]	46.2 (45.9)	8.47 (8.46)	21.73 (21.45)		164.8 (165.5)	37	6.9	22.3	7.842	1540
$CF_3C(O)N(Cl)C(O)F$	18.65 (18.62)	39.5 (39.3)	7.32 (7.24)	18.17 (18.32)		190.2 (193.5)	98	9.4	25.4	8.500	2083
$FC(O)N(Cl)C(O)F$	16.88 (16.72)	26.4 (26.5)	9.78 (9.76)	24.72 (24.74)		145.1 (143.5)	103	8.8	23.3	7.970	1913
$CF_3N(Cl)C(O)OSO_2F$	9.78 (9.79)	30.7 (31.0)	5.70 (5.71)	14.32 (14.28)	13.02 (13.06)	236.2 (245.5)	125	6.8	17.1	6.650	1500
$CF_3C(O)N(Cl)C(O)OSO_2F$	13.26 (13.16)	28.1 (27.8)	5.14 (5.12)	12.88 (12.98)	11.97 (11.70)		46[b]				
$FC(O)N(Cl)C(O)OSO_2F$	10.70 (10.74)	16.9 (17.0)	6.38 (6.26)	15.77 (15.88)	14.46 (14.32)		83[c]				
$CF_3N(H)C(O)F$						134 (131)	25[d]				
$CF_3C(O)N(H)C(O)F$							25[e]				
$FC(O)N(H)C(O)F$							25[f]				

[a] Calculated values in parentheses. [b] At 87 Torr. [c] At 161 Torr. [d] At 20 Torr. [e] At <1 Torr. Mp 36°. [f] At 2 Torr. Mp 19°.

Table III. Infrared and ^1H and ^{19}F Nmr Spectral Data

		Nmr[a]				
Compd	Infrared (cm^{-1})	δ(CF$_3$), ppm	δ(C(O)F), ppm	δ(S-F), ppm	δ(N-H), ppm	J, Hz
$CF_3N(Cl)C(O)F$	1868 vs, 1319 s, 1287 s, 1246 vs, 1212 vs, 1021 m, 978 m, 767 w, 738 m, 683 m	59.8 d[b]	8.1 q			16.2
$CF_3C(O)N(Cl)C(O)F$	1867 s, 1787 s, 1308 s, 1260 vs, 1237 s, 1217 s, 1154 m, 1131 m, 1052 w, 870 w, 744 m, 715 m	70.1 d[b]	1.1 q			9.5
$FC(O)N(Cl)C(O)F$	1908 m, 1868 vs, 1305 m, 1247 vs, 1060 w, 1020 w, 999 w, 735 m		2.3[b]			
$CF_3N(Cl)C(O)OSO_2F$	1832 vs, 1492 vs, 1315 s, 1295 vs, 1255 vs, 1215 vs, 975 s, 855 s, 821 m, 800 w	58.8 s[b]		−46.2 s		
$CF_3C(O)N(Cl)C(O)OSO_2F$[e]	1830 m, 1818 s, 1775 s, 1478 s, 1303 m, 1263 m, 1210 vs, 1125 m, 1008 m, 880 m, 848 m, 565 m	70.3 s[b]		−45.8 s		
$FC(O)N(Cl)C(O)OSO_2F$[e]	1878 m, 1857 s, 1815 s, 1480 s, 1275 m, 1240 s, 1215 s, 1000 m, 848 m, 733 w, 567 m		0.86 s[b]	−46.4 s		
$CF_3N(H)C(O)F$	3498 m, 1885 s, 1500 s, 1353 m, 1285 m, 1250 s, 1215 s, 1165 s, 1033 w, 1003 m, 920 w, 760 w, 745 w, 655 w	59.8 bs[b] 61.9 d[c]	6.3 bs 5.33 q		7.6 bs 7.2 s	 12 (F-F)
$CF_3C(O)N(H)C(O)F$	3460 w, 1905 s, 1863 m, 1800 m, 1511 s, 1282 s, 1185 s, 1120 s, 881 w	76.8 bs[b,d] 76.4 c[c]	−4.6 bs −5.9 c		10.4 bs 10.56 s	
$FC(O)N(H)C(O)F$	3480 vw, 2260 w, 1865 m, 1528 w, 1290 m, 1205 s, 1154 w, 1030 w, 980 w		−1.25[b,d]		8.7 s	

[a] Key: d, doublet; q, quartet; s, singlet; b, broad; c, complex. [b] At +20°. [c] At −20°. [d] 1:1 acetonitrile–trichlorofluoromethane solvent. [e] Thin film between AgCl disks.

of the products. Usually a twofold excess of ClF was used, whereas normally a 10% excess of isocyanate was used in the $ClOSO_2F$ reactions to ensure total consumption of the less volatile chlorine fluorosulfate. Addition of either ClF or $ClOSO_2F$ occurred in the liquid–liquid phase, and temperature and pressure conditions were adjusted accordingly. Low-pressure gas or gas–liquid reactions were attempted and found to be uniformly unsuccessful (Table II).

General Reaction Procedure for the *N*-Chloramine and HCl Reactions. After a 1.2-2-fold excess of HCl was condensed with the chloramine at −195° in a glass vessel, the mixture was warmed to 25° and was allowed to remain for a short time (Table I). The contents of the vessel were cooled to −78° and the chlorine and unreacted HCl were distilled away. Final purification was obtained by fractional condensation. These secondary amines are unstable in glass eliminating HF and the parent isocyanate and must be stored at lowered temperatures.

Results and Discussion

The reactions of ClF and $ClOSO_2F$ with perfluoroacyl isocyanates were straightforward 1,2 additions with no evidence of 1,4 addition. The other polar molecules, Cl_2O, CF_3OCl, ClNCO, $ClNSF_2$, and $ClNS(O)F_2$, were found not to add to the isocyanates under thermal conditions that were tried. When decomposed at 80°, the fluorosulfate addition compounds eliminate SO_3 to give the more stable ClF derivatives. The thermal decomposition of the latter compounds which occurred in excess of 100° was more complex to give the parent isocyanate, COF_2, COFCl, $COCl_2$, Cl_2, and other unidentified condensable and noncondensable products. With the exception of the ClNCO derivatives, the new chloramines were stable in Pyrex glass at 80° for 6 hr. The dichloramines $Cl_2NC(O)X$ (X = F, OSO_2F), which resulted in low-yield addition to ClNCO, are susceptible to photodecomposition[4] to form chlorine and the respective diazine.

The chloramines were observed to react with the sodium chloride disks of the infrared cell to produce chlorine, the parent isocyanate, and NaF or $NaOSO_2F$ on the disks. This behavior suggested the presence of a polarized nitrogen-chlorine bond $N^{\delta-}$-$Cl^{\delta+}$. As a result, the chloramines were allowed to react with hydrogen halides at about 0°, *i.e.*

$$\begin{array}{c} \mathrm{R_fN(Cl)C(O)R_f' + HX \rightarrow R_fN(H)C(O)R_f' + XCl} \\ \Big\downarrow{\scriptstyle 25^\circ \atop \scriptstyle \text{Pyrex}} \\ \mathrm{R_fNCO + HR_f'} \end{array}$$

where $R_f = CF_3, CF_3C(O), FC(O)$; $R_f' = F, OSO_2F$; and X = Cl, Br. It was possible to isolate the rather unstable secondary amines $R_fN(H)C(O)F$, formed from the ClF derivatives, but the secondary amines from the fluorosulfate derivatives were not found. The former was prepared also by the addition of hydrogen fluoride to the isocyanates.[17] Stabilities of the HF derivatives in Pyrex glass range from $CF_3N(H)C(O)F$ (6 hr) $\geqslant CF_3C(O)N(H)C(O)F \gg (FC(O))_2N(H)$ (5 min) for 50% decomposition at 25°. The compounds are in equilibrium with HF and the isocyanate. The glass container enhanced the decomposition and hydrolysis. $(FC(O))_2NH$, the least stable in glass, was quite stable in a Kel-F vessel resulting in only about 25% decomposition (CO_2, COF_2, FC(O)NCO, and solids) after thermolysis at 100° for 4 days. The condensation polymer $-[C(O)N(C(O)-)_2]_n$ expected from the elimination of HF did not form, but a solid which contained N-H and C-F as well as carbonyl stretching frequencies in the infrared spectrum was observed. The solid was probably $(FC(O))_2NH_2^+F^-$.

When reaction occurred between the chloramines and other compounds which contain negative chlorine, quantitative amounts of chlorine were invariably produced. However, it was only possible to isolate decomposition products of the suggested intermediate: $CF_3N(Cl)C(O)F + M\text{-}Cl \rightarrow [CF_3N(M)C(O)F] \rightarrow CF_3NCO + M\text{-}F + Cl_2$ ($M\text{-}Cl = BCl_3$, Al_2Cl_6, NaCl, $(CH_3)_3SiCl$; $M\text{-}Cl \neq CF_3SCl$, $CF_3C(O)Cl$, $HgCl_2$). The proposed unstable intermediate $CF_3N(M)C(O)F$ likely undergoes MF elimination to form the isocyanate. The elimination is enhanced by the formation of the stronger MF bond.

Electron impact mass spectral measurements at 70 and 17 eV contributed little to the confirmation of the structure of these compounds. The largest *m/e* observed, with the exception of the $CF_3C(O)$ group, was the parent isocyanate. The spectra of the chloramines were analogous to those of the isocyanate accompanied by chlorine-containing peaks. The $CF_3C(O)$ is anomalous with the CF_3 group also being removed making the $C(O)NCO^+$ a most distinctive peak. The chlorine fluorosulfate derivatives all showed an extremely intense CO_2 peak with very few mass fragments that could be attributed to the fluorosulfate group.

The ^{19}F nmr spectra of the ClF and $ClOSO_2F$ derivatives are typical (Table III). Coupling only occurs in $CF_3N(Cl)C(O)F$ and $CF_3C(O)N(Cl)C(O)F$ and no long-range coupling is observed in the fluorosulfate compounds. In the secondary amines both the fluorine and proton nmr resonances are broadened while in the analogous chloramines this effect is not observed. The proton resonances tend to become sharper and shift to lower field ($\Delta\delta = 0.4$–0.8 ppm) as the temperature is lowered from +20 to −20°. Broadened fluorine resonances (90 Hz in width) were observed at 25° and found to be also temperature dependent. Coupling of the fluorines on $CF_3N(H)C(O)F$ was resolved at −20° with no hydrogen coupling observed at that temperature. Variable-temperature nmr spectral studies of $CF_3C(O)N(H)C(O)F$ and $(FC(O))_2NH$ were restricted due to stability and solubility difficulties of the compounds.

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Registry No. $CF_3N(Cl)C(O)F$, 42016-31-9; $CF_3C(O)N(Cl)C(O)F$, 42016-32-0; FC(O)N(Cl)C(O)F, 42016-33-1; $CF_3N(Cl)C(O)OSO_2F$, 42016-34-2; $CF_3C(O)N(Cl)C(O)OSO_2F$, 42016-35-3; $FC(O)N(Cl)C(O)OSO_2F$, 42016-36-4; $CF_3N(H)C(O)F$, 3822-63-7; $CF_3C(O)N(H)C(O)F$, 42016-38-6; FC(O)N(H)C(O)F, 4386-60-1; CF_3NCO, 460-49-1; ClF, 7790-89-8; $CF_3C(O)NCO$, 14565-32-3; FC(O)NCO, 15435-14-0; ClNCO, 13858-09-8; $ClOSO_2F$, 13997-90-5; HCl, 7647-01-0.

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