reaction center is different, the $[Pd(dien)H_2O]^{2+}$ + RSR′ reaction provides the closest comparison.[9] In spite of the difference in charge, leaving group, and reaction center and the very large resultant difference in reactivity (6 orders of magnitude), the relative rates in both systems are reasonably similar. Neither shows any sensitivity to inductive effects and the relative rate constants are in the order $(CH_3)_2S$ (85) > $(C_2H_5)_2S$ (33) > $(n\text{-}C_4H_9)_2S$ (18) > $(i\text{-}C_3H_7)_2S$ (2.5) > $(sec\text{-}C_4H_9)_2S$ (1.0) for the palladium system and $(CH_3)_2S$ (104) > $(C_2H_5)_2S$ (55) > $(n\text{-}C_4H_9)_2S$ (35) > $(i\text{-}C_3H_7)_2S$ (2.4) > $(sec\text{-}C_4H_9)_2S$ (1.0) for the platinum complex. Since the dimensions of Pd(II) and Pt(II) are essentially the same,[14] this suggests a close similarity of the intimate mechanism of the two processes.

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Registry No. $Pt(dien)Br^+$, 15522-24-4; $(CH_3)_2S$, 75-18-3; $(C_2H_5)(CH_3)S$, 624-89-5; $(C_2H_5)_2S$, 352-93-2; $(\beta\text{-}ClC_2H_4)(CH_3)S$, 542-81-4; $(i\text{-}C_3H_7)_2S$, 625-80-9; $(n\text{-}C_4H_9)_2S$, 544-40-1; $(sec\text{-}C_4H_9)_2S$, 626-26-6; $(CH_2)_4S$, 110-01-0; thioxane, 505-29-3.

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Oxidation Reactions of Perfluoro(methanimine) and Related Compounds. Electrophilic Additions to $CF_2{=}NF$ and Fluoride-Promoted Oxidation of Perhalo Imines and Nitriles by Cl_2 and Br_2

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Reactions of $CF_2{=}NF$ with $S_2O_6F_2$, $BrOSO_2F$, $ClOSO_2F$, CF_3OF, CF_3OCl, $FOSO_2F$, Cl_2, Br_2, and I_2 were carried out. The electrophilic halides and pseudohalide $XOSO_2F$ (X = Cl, Br, OSO_2F) add in high yield to form FSO_2OCF_2NFX. The other reagents are unreactive under the same conditions, and only $FOSO_2F$ resulted in a small yield of the addition product $FSO_2OCF_2NF_2$ on heating. The in situ formation of CF_3NF^- from $CF_2{=}NF$ and MF (M = K, Cs) in the presence of Cl_2 and Br_2 results in the formation of CF_3NXF (X = Cl, Br). These reactions were extended with Br_2 to the imines $CF_3CF{=}NF$ and $C_2F_5CF{=}NF$ with similar results. With the nitriles CF_3CN and XCN (X = Cl, Br), reactions of Cl_2 in the presence of MF results in chlorofluorinations forming $C_2F_5NCl_2$, $C_2F_5N{=}NC_2F_5$, and CF_3NCl_2, respectively. With Br_2, bromofluorination is observed, forming $CF_3CF{=}NBr$, $C_2F_5N{=}NC_2F_5$, and $CF_3N{=}NCF_3$ as the respective products.

Introduction

The oxidation of fluorinated compounds containing carbon–nitrogen multiple bonds by halogens has been studied by many investigators. Earlier work on the direct fluorination of fluorocarbon nitriles, dinitriles, and other related compounds at higher temperatures led to a variety of interesting products, including in some cases products resulting from the simple addition of fluorine to the C–N multiple bonds (eq 1 and 2).[2-4]

$$ClCF_2C{\equiv}N \xrightarrow[140\ ^\circ C]{F_2/N_2} ClCF_2CF_2NF_2 + \text{others} \qquad (1)$$

$$N{\equiv}CCF_2C{\equiv}N \xrightarrow[160\ ^\circ C]{F_2/N_2} F_2NCF_2CF_2CF_2NF_2 + \text{others} \qquad (2)$$

In general, these reactions are low yield and lead to many different products resulting from bond cleavage. Subsequently, it was shown that CsF catalyzed the low-temperature addition of fluorine to fluorocarbon nitriles[5] and that certain fluorinated imines would add fluorine directly without apparent catalysis (eq 3 and 4).[6]

$$R_fC{\equiv}N + 2F_2 \xrightarrow[-78\ ^\circ C]{CsF} R_fCF_2NF_2 \qquad (3)$$

$$R_fN{=}CF_2 + F_2 \xrightarrow{-195\ \text{to}\ +25\ ^\circ C} R_fNFCF_3 \qquad (4)$$

Chlorine monofluoride has also been shown to add readily to almost any fluorinated compound containing a carbon–nitrogen double or triple bond.[7-11] Thus nitriles react at low temperatures to add 2 mol of ClF, and a variety of imines add ClF (eq 5–7). However, some reactions of ClF with imines require a CsF catalyst (eq 8).[12] Similarly, certain perfluoroalkylnitriles undergo low-yield chlorofluorination or bromofluorination on heating with metal fluorides (AgF, PbF_2, KF) and halogen (eq 9–11)[13] Finally, $ClOSO_2F$ has also been

$$R_fC{\equiv}N + 2ClF \xrightarrow{-78\ \text{to}\ 0\ ^\circ C} R_fCF_2NCl_2 \qquad (5)$$

$$R_fN{=}C{=}O + ClF \xrightarrow{-78\ ^\circ C} R_fNClC(O)F \qquad (6)$$

$$\begin{gathered} RN{=}CR_1R_2 + ClF \xrightarrow{-20\ ^\circ C} RNClCFR_1R_2 \\ (R, R_1, R_2 = R_f, F, Cl) \end{gathered} \qquad (7)$$

$$CF_3SF_4N{=}CFCF_3 + ClF \xrightarrow[25\ ^\circ C]{CsF} CF_3SF_4NClCF_2CF_3 \qquad (8)$$

$$CF_3CN \xrightarrow[50\text{–}75\ ^\circ C]{Cl_2,\ AgF} CF_3CF_2NCl_2 + \text{others} \qquad (9)$$

$$CF_3CN \xrightarrow[100\text{–}200^\circ C]{Cl_2,\ KF\ \text{or}\ PbF_2} CF_3CF{=}NCl + \text{others} \qquad (10)$$

$$CF_3CN \xrightarrow[100\text{–}190\ ^\circ C]{Br_2,\ AgF} CF_3CF{=}NBr + \text{others} \qquad (11)$$

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demonstrated to add readily to C=N bonds (eq 12 and 13).[14,15]

$$R_fN{=}C{=}O + ClOSO_2F \xrightarrow{-78 \text{ to } +25\ °C} R_fNClC(O)OSO_2F \quad (12)$$

$$C_2F_5N{=}CF_2 + ClOSO_2F \xrightarrow{-78\ °C} C_2F_5NClCF_2OSO_2F \quad (13)$$

In the above work, free-radical additions with fluorinated nitriles and imines, other than higher temperature reactions with F_2, are rare. However, the pseudohalogen $S_2O_6F_2$ will add to certain nitriles (eq 14).[16]

$$CF_3C{\equiv}N + 2S_2O_6F_2 \xrightarrow{80\ °C} CF_3C(OSO_2F)_2N(OSO_2F)_2 \quad (14)$$

In continuing investigations on the chemistry of the simplest perfluoro imine, $CF_2{=}NF$, we undertook an investigation of its reaction chemistry with halogens and reactive halogen compounds. Both F_2 and ClF had been previously shown to add to $CF_2{=}NF$ in high yield,[6,9] and reactions of $CF_2{=}NF$ with Cl_2, Br_2, I_2, CF_3OCl, CF_3OF, and $XOSO_2F$ (X = F, Cl, Br) were investigated. Fluoride-promoted reactions of $CF_2{=}NF$ with X_2 (X = Cl, Br, I) were also investigated and extended to $R_fCF{=}NF$ (R_f = CF_3, C_2F_5), CF_3CN, and XCN (X = Cl, Br).

Experimental Section

General Considerations. All work was carried out in Pyrex or stainless steel (304 and 316) vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured on a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by *PVT* measurements.

IR spectra were taken on a Perkin-Elmer 337, 1330, or 180 spectrometer. A 10-cm glass cell fitted with a AgCl, KCl, or CsI window was employed. NMR spectra were recorded on a Varian XL-100-15 spectrometer using ~80 mol % $CFCl_3$ as solvent and internal reference. High-field chemical shifts are negative and vice versa. Mass spectra were taken on a Finnigan 4021-C instrument at 70 eV for EI and CI (CH_4). Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by the method of Kellogg and Cady[17] or by the use of a small isoteniscope.[18] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, GLC was carried out on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 10 ft × $^3/_8$ in. or 20 ft × $^1/_4$ in. column packed with ~35% Halorcarbon 11-21 polymer oil or perfluoro(tributylamine) on acid-washed Chromosorb P was used.

Reagents. The chemicals I_2, Br_2, Cl_2, F_2, CsF, KF, SO_3, CF_3CN, C_2F_5CN, ClCN, and BrCN were obtained from commercial sources and appropriately purified before use. The compounds $BrOSO_2F$,[19] $ClOSO_2F$,[20] $S_2O_6F_2$,[21] $CF_2{=}NF$,[22] $CF_3CF{=}NF$,[22] $C_2F_5CF{=}NF$,[22] CF_3NClF,[23] CF_3OCl,[24] CF_3OF,[25] and $FOSO_2F$[26] were prepared by literature methods. Chlorine monofluoride was prepared by reaction of equimolar amounts of Cl_2 and F_2 in a Monel bomb at 250 °C. *Caution*! Many of the compounds employed in this work are probably rather toxic, many are very aggressive oxidizers, and some are explosive. Due caution must be exercised in handling these materials.

Table I. Addition Reactions to $CF_2{=}NF$

reactant[a]	conditions (°C, h)[b]	products (% yield)[c]
$S_2O_6F_2$	22, 2	$FSO_2OCF_2N(F)OSO_2F$ (98)
$ClOSO_2F$	22, 4	FSO_2OCF_2NClF (85)
$ClOSO_2F$	22, 48	FSO_2OCF_2NClF (85)
$BrOSO_2F$	22, 5	FSO_2OCF_2NBrF (85)
CF_3OF	22, 66	no reacn
CF_3OF	120, 3	no reacn
CF_3OF	150, 3	COF_2, N_2, SiF_4, CF_3OCF_3[27]
CF_3OCl	22, 84	CF_3NClF[23] (62), COF_2, CF_3OCl, CF_2NF
$FOSO_2F$	22, 12	no reacn
$FOSO_2F$	65, 3	$FSO_2OCF_2NF_2$ (15), N_2, CF_3OSO_2F[28] (64), $CF_2(OSO_2F)_2$[29] (9)
Cl_2	22, 23	no reacn
Cl_2	22, 17 (UV)	no reacn
Br_2	22, 10	no reacn
Br_2	22, 3 (UV)	no reacn
I_2	22, 12	no reacn

[a] Equimolar amounts of $CF_2{=}NF$ and reactant on a 1–5-mmol scale. [b] See Experimental Section under Reactions. [c] % yield based on starting $CF_2{=}NF$. Small amounts of products other than those listed were present but were not identified.

Reactions. The addition reactions of $BrOSO_2F$, $ClOSO_2F$, and $S_2O_6F_2$ were carried out in a 250-mL glass reactor fitted with a cold finger and glass–Teflon valves. $CF_2{=}NF$ was condensed into the cold finger at −196 °C by vacuum transfer. The valve was closed, and then the bottom of the large bulb was cooled to −196 °C and the fluorosulfate was added. The cold finger valve was then opened, and the reactor was allowed to warm in air to 22 °C. Other addition reactions were carried out in a 100-mL glass reactor fitted with a glass–Teflon valve. $CF_2{=}NF$ was condensed into the bottom of the reactor at −196 °C, followed by the other reactant on the upper walls. The vessel was then warmed at 22 °C over a period of 30 min or held at another low temperature for a time. After the reactions were complete, the reactor contents were cooled to −196 °C and allowed to distill through a series of cold traps under dynamic vacuum as the reactor warmed slowly in the air. The addition reactions are summarized in Table I.

Metal fluoride promoted reactions were carried out in 100-mL glass reactors fitted with glass–Teflon valves and containing a small stirring bar. Metal fluoride, which had been fused and ground to a fine powder in a drybox, was added to the reactor in the drybox. The reactor was then evacuated and cooled to −196 °C. The appropriate reactants were added by vacuum transfer, and the reactor was then warmed to 22 °C and stirred for an appropriate time. The reactor contents were then separated as in the addition reactions. The metal fluoride promoted reactions are summarized in Table II. Characterization of new compounds from all reactions follows. The known products were identified by IR and in most cases also by mass spectra or ^{19}F NMR or both.

$F^{M}O_2SOCF^{A}F^{B}NF^{X}OSO_2F^{N}$: mp −89 °C; mol wt 278.7 (calcd 281.14); NMR M δ 50.1 (dt), N 41.1 (dd), A −79.4 (m), B −78.4 (m), X −14.1 (br s) (J_{AB} = 98, $J_{AM} = J_{BM}$ = 7.5 $J_{AX} \simeq J_{BX} \simeq$ 3.5,

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Table II. Fluoride-Promoted Reactions of Imines and Nitriles with Halogens

reactants (amt, mmol)	MF (amt, mmol)^c	conditions (°C, h)^a	products (yield, mmol)^b
CF_2=NF (3.0), Cl_2 (3.0)	KF (8)	22, 20	CF_3NClF^{23} (1.6), Cl_2, CF_2=NF
CF_2=NF (1.2), Cl_2 (2.3)	CsF (10)	22, 14	CF_3NClF (0.7), Cl_2, CF_2=NF
CF_2=NF (11.7), Br_2 (14.0)	KF (6.2)	22, 21	CF_3NBrF (6.1), Br_2, CF_2=NF
CF_2=NF (4.8), Br_2 (7.0)	CsF (6.1)	22, 12	CF_3NBrF (2.8), Br_2, CF_2=NF
CF_2=NF (3.0), I_2 (4.0)	KF (3.8)	22, 21	CF_3NFCF=NF^{30} (1.1), I_2, CF_2=NF
CF_3CF=NF (2.6), Br_2 (3.0)	CsF (5.3)	22, 18	C_2F_5NBrF (1.1), Br_2, CF_3CF=NF^{22}
CF_2=NF (2.0), CF_3OF (1.9)	KF (1.0)	22, 9	$CF_3NF_2{}^{31}$ (~1.5), $CF_3NFC(O)F^{32}$ (~0.5), CF_3OF, COF_2
CF_3CF_2CF=NF (1.5), Br_2 (2.0)	CsF (1.0)	22, 7	C_3F_7NBrF (0.3), C_3F_7N=NC_3F_7,^{13} Br_2, CF_3CF_2CF=NF^{22}
CF_3CN (3.0), Cl_2 (3.0)	CsF (3.6)	22, 22	$C_2F_5NCl_2{}^7$ (0.2), Cl_2, CF_3CN
CF_3CN (3.0), Cl_2 (6.0)	CsF (3.6)	22, 70	$C_2F_5NCl_2$ (0.9), Cl_2, C_2F_5N=NC_2F_5 (0.6)^{13}
CF_3CN (4.0), Br_2 (4.4)	CsF (7.2)	22, 20	CF_3CF=NBr^{13} (0.4), CF_3CN, Br_2, C_2F_5N=NC_2F_5
CF_3CN (4.0), Br_2 (8.4)	CsF (7.2)	22, 68	CF_3CF=NBr (1.9), Br_2, CF_3CN, C_2F_5N=NC_2F_5 (0.3)
ClCN (3.0), Cl_2 (6.0)	CsF (10.2)	22, 12	$CF_3NCl_2{}^7$ (0.6), Cl_2, ClCN
ClCN (2.1), Cl_2 (4.2)	CsF (10.2)	55, 4	CF_3NCl_2 (0.8), Cl_2, ClCN
BrCN (7.4), Br_2 (8.9)	CsF (2.3)	22, 20	CF_3N=$NCF_3{}^{13}$ (0.3), Br_2, BrCN, others

^{a} See Experimental Section under Reactions. ^{b} Small amounts of other products were often present but were not identified. ^{c} In all reactions except those with I_2, the MF was partially converted to MX (X = Cl, Br) and considerable X_2 was absorbed on the MF/MX mixture at 22 °C, especially with M = Cs.

$J_{XM} = 1.5$, $J_{BN} = 1.0$, $J_{XN} = 4.5$, $J_{NA} \simeq 0$ Hz); IR 1850 (w), 1500 (vs), 1272 (vs), 1250 (vs), 1217 (s), 1188 (w), 1159 (vs), 1116 (m), 1100 (w), 1020 (m), 990 (s), 942 (m), 920 (m), 841 (s), 776 (m), 733 (w), 718 (w), 599 (w), 566 (m) cm^{-1}; major *m/z* (EI) 182 ($CF_4NO_3S^+$), 149 ($CF_3SO_3{}^+$), 85 (CF_3O^+), 83 ($FSO_2{}^+$ or CF_3N^+), 69 ($CF_3{}^+$), 67 (FSO^+), 64 ($SO_2{}^+$), 50 ($CF_2{}^+$), 48 (SO^+), 47 (CFO^+), 44 (CFN^+); major *m/z* (CI, 140–400) 262 ($MH^+ - HF$), 216 (?), 183 ($CF_4NO_3SH^+$), 182 ($CF_4NO_3S^+$), 164 ($CF_3NO_3SH^+$), 149 ($CF_3SO_3{}^+$).

$F^{M}O_2SOCF^{A}F^{B}NClF^{X}$: mp <−120 °C; mol wt 217.5 (calcd 216.5); NMR M δ 48.5 (dd), A −76.6 (m), B −77.7 (m), X −3.6 (br s) ($J_{AB} = 97.0$, $J_{AM} = J_{BM} = 8.0$, $J_{MX} = 2.5$, $J_{AX} \simeq J_{BX} = 12.0$ Hz); IR 2742 (vw), 1878 (vw), 1491 (vs), 1240–1270 (vs), 1201 (vs), 1115–1150 (vs), 954 (vs), 917 (s), 839 (vs), 780 (sh), 762 (m), 733 (sh), 688 (w), 636 (m), 595 (s), 578 (sh), 520 (m) cm^{-1}; major *m/z* (EI) 149 ($CF_3O_3S^+$), 120/118 (CF_3ClN^+), 101/99 (CF_2ClN^+), 85 (CF_3O^+), 83 (CF_3N^+ or $FSO_2{}^+$), 80 ($SO_3{}^+$), 70/68 ($NFCl^+$), 69 ($CF_3{}^+$), 67 (FSO^+), 64 ($SO_2{}^+$); major *m/z* (CI) 120/118 ($MH^+ - HOSO_2F$), 84 (CF_3NH^+ or FO_2SH^+).

$F^{M}O_2SOCF^{A}F^{B}NBrF^{X}$: bp 91.6 °C; mp −97 °C; mol wt 262.0 (calcd 261.98); log *P* (torr) = 8.2364 − 1953.7/*T*; $\Delta H_{vap} = 8.94$ kcal/mol; $\Delta S_{vap} = 24.5$ eu; NMR M δ 48.1 (td), A −75.0 (m), B −75.9 (m), X −13.8 (br m) ($J_{AB} = 95.0$, $J_{AM} = J_{BM} = 7.8$, $J_{MX} = 2.0$, $J_{BX} = J_{AX} = 20.0$ Hz); IR 1500 (s), 1384 (w), 1364 (w), 1250 (vs), 1199 (vs), 1112 (vs), 950 (s), 917 (s), 838 (s), 783 (m), 747 (m), 671 (w), 624 (m), 584 (m), 556 (m), 509 (w) cm^{-1}; major *m/z* (CI) 183 ($MH^+ - Br$), 149 ($CF_3SO_3{}^+$), 118 ($F_2SO_3{}^+$), 84 (CF_3NH^+ or FSO_2H^+).

$F^{A}O_2SOCF_2{}^{B}NF_2{}^{C}$. This compound was not isolated pure and is characterized only by its NMR spectrum: A δ 49.5 (tt), B −82.5 (d), C 21.2 (br s) ($J_{AB} = 7.5$, $J_{AC} = 7.5$, $J_{AC} = 1.5$, $J_{BC} < 1.0$ Hz).

$CF_3{}^{A}NBrF^{X}$: bp −2.8 °C; mp −90 °C; mol wt 182.8 (calcd 181.92); log *P* (torr) = 7.6820 − 1298.2/*T*; $\Delta H_{vap} = 5.94$ kcal/mol; ΔS_{vap} 22.0 eu; NMR A δ −77.6 (d), X −16.5 (br s) ($J_{AX} = 14.5$ Hz); IR 1365 (w), 1245 (vs), 1238 (vs), 1198 (vs), 1031 (w), 934 (s), 872 (m), 731 (s), 579 (w), 516 (w) cm^{-}1; major *m/z* (EI) 183/181 (M^+), 95/93 (NBr^+), 81/79 (Br^+), 69 ($CF_3{}^+$), 64 (CF_2N^+), 50 ($CF_2{}^+$); major *m/z* (CI) 183/181 (M^+), 164/162 ($M - F^+$), 145/143 (CF_2NBr^+), 103 (CF_4NH^+), 95/93 (NBr^+), 84 (CF_3NH^+), 83 (CF_3N^+), 81/79 (Br^+).

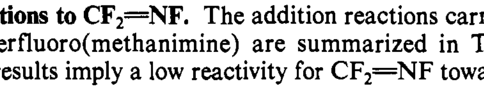
$CF_3{}^{M}CF^{A}F^{B}NBrF^{X}$: bp 27.5 °C; mp −98 °C; mol wt 231.9 (calcd 231.93); log *P* (torr) = 7.8931 − 1507.0/*T*; $\Delta H_{vap} = 6.90$ kcal/mol; $\Delta S_{vap} = 22.9$ eu; NMR M δ −80.6 (dd), A −111.9 (m), B −103.9 (m), X −17.1 (br d) ($J_{AB} = 202$, $J_{AM} = 1.0$, $J_{BM} \simeq 0$, $J_{AX} = 9.5$, $J_{BX} = 57.0$, $J_{MX} = 13.0$ Hz); IR 1553 (w), 1348 (s), 1224 (vs), 1167 (s), 1073 (s), 921 (m), 794 (w), 765 (w), 736 (sh), 711 (m), 682 (m), 613 (m), 566 (w), 534 (w) cm^{-1}; major *m/z* (EI) 233/231 (M^+), 164/162 (CF_3NBr^+), 145/143 (CF_2NBr^+), 119 ($C_2F_5{}^+$), 114 ($C_2F_4N^+$), 100 ($C_2F_4{}^+$), 95/93 (NBr^+), 81 ($C_2F_3{}^+$), 69 ($CF_3{}^+$), 50 ($CF_2{}^+$).

$CF_3{}^{M}CF_2{}^{N}CF^{A}F^{B}NBrF^{X}$. This compound could not be separated from small amounts of C_3F_7N=NC_3F_7 by GLC due to decomposition. Therefore, the NMR, IR, and mass spectra were obtained on impure samples and some of the IR absorptions and MS values might be due to C_3F_7N=NC_3F_7: NMR M δ −82.2 (m), N −124.8 (dm), A −108.7 (br m), B −99.9 (br m), X −16.5 (br d) ($J_{AB} = 204$, $J_{AX} < 15$, $J_{BX} = 60$, J_{AM} or $J_{XM} = 3.5$ or 8.0, J_{AN} or $J_{BN} \simeq 2$, $J_{MN} \simeq 0$, $J_{XN} = 17.0$ Hz); IR 1340 (w), 1283 (m), 1240 (vs), 1204 (m), 1143 (w), 1120 (w), 1075 (vw), 1057 (vw), 1020 (w); 996 (m), 980 (sh), 923 (w), 831 (w), 730 (m), 690 (vw), 640 (vw), 582 (w) cm^{-1}; major *m/z* (EI) 283/281 (M^+), 169 ($C_3F_7{}^+$), 119 ($C_2F_5{}^+$), 114 ($C_2F_4N^+$), 100 ($C_2F_4{}^+$), 95/93 (NBr^+), 92 (?), 69 ($CF_3{}^+$); major *m/z* (CI) 284/282 (MH^+), 264/262 ($M - F^+$), 204 ($C_3F_8NH_2{}^+$), 202 ($C_3F_8N^+$), 200 (?), 184 ($C_3F_7N^+$), 169 ($C_3F_7{}^+$), 119 ($C_2F_5{}^+$), 109/107 ($CNBrH^+$).

$CF_3{}^{A}CF^{B}$=NBr. This compound has been previously reported, but only an incomplete IR spectrum was given along with mention of M^+ ions at 193 and 195 in the mass spectrum:[13] NMR A δ −71.8 (d), B −27.5 (br q) ($J_{AB} = 5.5$ Hz); IR 1700 (s), 1640 (sh), 1340 (vs), 1230 (vs), 1185 (vs), 1112 (vs), 1020 (vw), 832 (m), 730 (m), 700 (w), 659 (s), 570 (w) cm^{-1}.

Results and Discussion

Additions to CF_2=NF. The addition reactions carried out with perfluoro(methanimine) are summarized in Table I. These results imply a low reactivity for CF_2=NF toward free radicals, compared to that for fluoroolefins such as C_2F_4, which readily add Cl_2, Br_2, $CF_3O_3CF_3$,[33] and FSO_2OF[34] under very mild conditions. However, the addition of F_2 to CF_2=NF, as well as the addition of FSO_2OF and possibly $S_2O_6F_2$, shows that free-radical additions are possible. The reactions with CF_3OF did not occur readily below 150 °C, and the failure to isolate the addition compound may be a consequence of this high reaction temperature. The observed products other than the addition compound with both FSO_2OF and CF_3OF are in fact very similar and could arise by the same path (eq 15).



(15)

(R = FSO_2, CF_3)

The amount of $(RO)_2CF_2{}^{35}$ in the case of R = CF_3, if formed,

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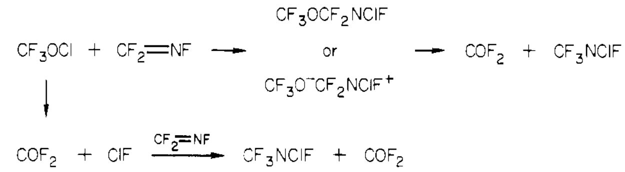
(33) Hohorst, F. A.; Paukstelis, J. V.; DesMarteau, D. D. *J. Org. Chem.* **1974**, *39*, 1298.

(34) Gilbreath, W. L.; Cady, G. H. *Inorg. Chem.* **1963**, *2*, 496.

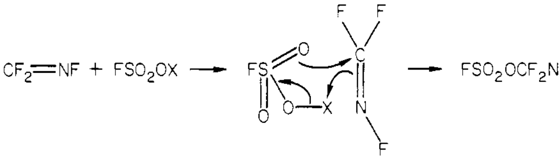
Scheme I



was very small. Faint signals in the NMR spectrum had chemical shifts close to those of $(CF_3O)_2CF_2$, but it cannot be concluded that the compound was definitely present.

The unsuccessful attempt to add Br_2 and I_2 to $CF_2{=}NF$ is not surprising, because the reverse reaction would probably be favored. In the case of Cl_2, however, the addition product $ClCF_2NClF$, which can be prepared by reaction of ClF and F_2 with ClCN, is stable to at least 100 °C.[36] Obviously, the lack of reactivity with Cl_2 is related to other factors.

In contrast to the above, $CF_2{=}NF$ readily adds both of the very electrophilic halogen reagents FSO_2OBr and FSO_2OCl at or below 22 °C. The facile addition of $S_2O_6F_2$ under the same conditions leads us to speculate that these three reactions are mechanistically the same and could occur in a highly concerted manner (eq 16).[37] The reaction with CF_3OCl



(16)

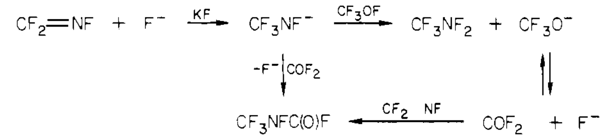
(X = Cl, Br, FSO_2)

represents a case of only a moderately electrophilic halogen derivative.[38] As such, its rate of reaction with $CF_2{=}NF$ was very slow at 22 °C and the possibility exists that it does not react at all. The observed chlorofluorination may derive from the slow decomposition of CF_3OCl to ClF and COF_2. In any case, the observed products can be explained via Scheme I.

The decomposition of a CF_3O– derivative can occur readily in some compounds, but it is rather unexpected for a CF_3O–C derivative.[39] If the reaction is a two-step ionic mechanism, then the CF_3O^- may lose F^- and give the observed product. Chlorofluorination by CF_3OCl is observed in additions to olefins.[40] Normally, CF_3OCl is quite stable at 22 °C in properly passivated containers, but it is quite sensitive to traces of H_2O and other impurities, which can promote its decomposition to COF_2 and ClF. The latter is probably the most likely path for the formation of CF_3NClF and COF_2.

Fluoride-Promoted Oxidations. In the previous section, the lack of reactivity of $CF_2{=}NF$ toward Cl_2, Br_2, and I_2 was noted, whereas strong polar electrophiles were very reactive. If one activated the C=N bond by making the nitrogen more nucleophilic, then less electrophilic halogens might react. One way to accomplish this is to form a nitrogen-centered anion. This is a very facile process with $CF_2{=}NF$ and metal fluorides,[30] and the system $CF_2{=}NF/X_2/MF$ (X = Cl, Br; M = K, Cs) was investigated. The success of this work then prompted us to look at similar reactions with some other perhalo imines and nitriles.

Scheme II



The fluoride-promoted oxidations of imines and nitriles are summarized in Table II. The reactions with $CF_2{=}NF$ are easily rationalized as shown in eq 17. Clearly, both CsF and

$$CF_2{=}NF + MF \xrightarrow{22\ °C} M^+CF_3NF^- \xrightarrow[22\ °C]{X_2} MX + CF_3NFX \quad (17)$$

KF are equally effective fluoride sources and Cl_2 and Br_2 are sufficiently strong oxidants, whereas I_2 is not. The formation of MX may be a fortuitous benefit, because it decreases the fluoride ion activity in these heterogeneous reactions and minimizes any competing reactions. Perfluoro(methanimine) reacts very readily with itself in the presence of KF or CsF to form $CF_3NFCF{=}NF$ and $CF_3\overline{NCF_2N}F$, respectively.[30] The absence of these products and the material balance show that all the CF_3NF^- formed is oxidized by halogen. This must be due to a large difference in reaction rates with $X_2 >> CF_2{=}NF$ under the experimental conditions.

The reaction of CF_3OF with $CF_2{=}NF$ in the presence of KF is interesting. As stated in the previous section, CF_3OF and $CF_2{=}NF$ alone do not react at 22 °C. In the presence of KF, however, CF_3OF will oxidize the CF_3NF^- ion to CF_3NF_2. The observed products can be rationalized by Scheme II. A related reaction has been observed for $KOC(CF_3)_3$ with CF_3OF, forming $KOCF_3$ and $(CF_3)_3COF$.[41]

The reactions with $R_fCF{=}NF$ clearly proceed in a manner analogous to that of $CF_2{=}NF$ with CsF/Br_2 (eq 18; $R_f = CF_3$,

$$R_fCF{=}NF + CsF \xrightarrow{22\ °C} Cs^+R_fCF_2NF^- \xrightarrow[22\ °C]{Br_2} CsBr + R_fCF_2NBrF \quad (18)$$

C_2F_5). The yields compared to that for $CF_2{=}NF$ decrease considerably with larger R_f groups, and the stability of $CF_3CF_2CF_2NBrF$ is marginal at 22 °C. The diazene formed in this reaction presumably arises by the decomposition of the *N*-bromo compound. Although Cl_2 was not tried in these reactions, it seems safe to assume that it would be equally or perhaps more effective in the formation of the known stable compounds CF_3CF_2NClF and $CF_3CF_2CF_2NClF$.[36]

The above work with imines suggested that nitriles should also react. Indeed, the work cited in the Introduction had already shown this to be possible.[13] However, most of this work was done with AgF and X_2 at elevated temperatures and it is possible under these conditions that the reacting species might be XF rather than X_2.[42] The reactions with CF_3CN clearly suggest that the same type intermediates can be postulated in these reactions as in those with $CF_2{=}NF$ and $R_fCF{=}NF$ (eq 19; X = Cl, Br). From the results in Table

$$\begin{gathered} CF_3CN + CsF \xrightarrow{22\ °C} CF_3CF{=}N^-Cs^+ \xrightarrow{X_2} \\ CF_3CF{=}NX + CsX \xrightarrow{CsF} CF_3CF_2{-}NX^-Cs^+ \xrightarrow{X_2} CsX + CF_3CF_2NX_2 \quad (19) \end{gathered}$$

II it seems clear that oxidation of $CF_3CF{=}NCl$ by Cl_2 is faster than that of $CF_3CF{=}NBr$ by Br_2, because no $CF_3CF{=}NCl$ is isolated. It also follows that $CF_3CF_2NCl_2$ is more stable than $CF_3CF_2NBr_2$, which is not observed, and both *N*,*N*-dihalo compounds decompose to the corresponding diazene $C_2F_5N{=}NC_2F_5$.[43]

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(35) Berenblit, V. V.; Sass, V. P.; Senyvehov, L. N.; Starobin, Yu. A. *J. Org. Chem. USSR (Engl. Transl.)* **1976**, *12*, 765.

(36) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1981**, *20*, 1.

(37) This type of reaction has been proposed for the additions to olefins of the related compounds CF_3SO_2O-X (X = Cl, Br). Unpublished work with $BrOSO_2F$ also shows it behaves in the same way. Katsuhara, Y.; DesMarteau, D. D. *J. Org. Chem.* **1980**, *45*, 2441.

(38) The chlorine in CF_3OCl is electrophilic, but it does not compare in this sense to halogen in $XOSO_2F$ (X = Cl, Br).

(39) Bernstein, P. A.; DesMarteau, D. D. *J. Fluorine Chem.* **1972**, *2*, 315.

(40) Johri, K. K.; DesMarteau, D. D. *J. Org. Chem.*, in press.

(41) Walker, N.; DesMarteau, D. D. *J. Fluorine Chem.* **1975**, *5*, 127.

(42) Sharts, C. M.; Sheppard, W. A. *Org. React. (N.Y.)* **1974**, *21*, 125.

The reactions of XCN are very similar to the above except that at some point the original C–X bond is converted to a C–F bond. The failure to isolate either $CF_2{=}NCl$ or $CF_2{=}NBr$ shows that their conversion to CF_3NX_2 is fast relative to their rate of formation and the product in the case of Br_2 is completely converted to the diazene (eq 20; X = Cl, Br).

$$XC{\equiv}N \xrightarrow[22\ ^\circ C]{CsF/X_2} XCF{=}NX \text{ or } CF_2{=}NX \xrightarrow[22\ ^\circ C]{CsF,\ X_2} CF_3NX_2 \xrightarrow{(X\ =\ Br)} CF_3N{=}NCF_3 \quad (20)$$

Characterization of New Compounds. The data given in the Experimental Section provide convincing proof of structure for the new compounds FSO_2OCF_2NFX (X = F, Cl, Br, OSO_2F) and R_fNBrF (R_f = CF_3, C_2F_5, C_3F_7) and additional data for $CF_3CF{=}NBr$. The CI or EI mass spectra contain intense molecular ions for R_fNBrF. For FSO_2OCF_2NFX, the CI spectra contain ions corresponding to the loss of $HOSO_2F$ and HF from MH^+ for X = Cl and OSO_2F, respectively. A weak molecular ion MH^+ was also present in the CI spectrum of FSO_2OCF_2NFCl. For FSO_2OCF_2NBrF, the CI mass spectrum indicated the loss of Br· from the MH^+ molecular ion, resulting in an intense $FSO_2OCF_2NFH^+$ ion.

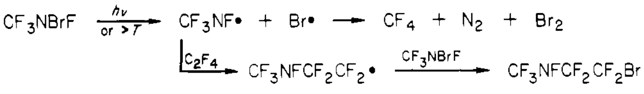
The infrared spectra of FSO_2OCF_2NFX (X = Cl, Br, OSO_2F) contain strong absorptions at ~1500 cm^{-1} due to $\nu_{antisym}(SO_2)$ and 1250–1272 cm^{-1} for $\nu_{sym}(SO_2)$. Two strong absorptions in the 1100–1220-cm^{-1} region for each compound are due to the two expected $\nu(CF_2)$ stretches. Other bands in the 700–1100-cm^{-1} region are reasonable in terms of C–O, S–F, C–N, S–O, and N–X stretches, but these cannot be readily assigned. For R_fNBrF, the spectra are as expected for a fluorocarbon derivative and a detailed assignment of the infrared and Raman spectra of CF_3NBrF will be reported separately.[44]

The ^{19}F NMR results are particularly definitive for the new compounds. Except for CF_3NBrF and $FSO_2OCF_2NF_2$, all the new compounds are of the type $RCF^AF^BNF^XX$ and exhibit the expected second-order ABX spin system.[9,36] The signal for F^X is rather broad in every case as expected for molecules of this type.[45] The J_{AB} values for FSO_2OCF_2NFX (X = Cl, Br, OSO_2F) are all ~100 Hz, and those for R_fCF_2NBrF (R_f = CF_3, C_2F_5) are ~200 Hz. These values are comparable to those of other related compounds of the type R_fCF_2NClF and XCF_2NClF, which have J_{AB} values in the range of 128–204 Hz.[36] The J_{AX} and J_{BX} values vary widely from ~60 to ~3 Hz. This variation may be explicable in terms of the rotamer population. In CF_3NBrF, $^3J_{FF}$ = 14.5 Hz, which probably represents an average value for a freely rotating CF_3 group ($^3J_{FF}$ in CF_3NClF is 9.9 Hz[3]). In FSO_2OCF_2NFX (X = Cl, Br), the $^3J_{FF}$ values (12 and 20 Hz, respectively) would imply rotamer populations similar to those of CF_3NFX (X = Cl, Br). The large J_{BX} (~60 Hz) and small J_{AX} (~10 Hz) in $R_fCF^AF^BNFX$ (X = Cl,[9,36] Br) may be consistent with a predominance of gauche BX and trans AX fluorines in the rotamer populations.

In $FSO_2OCF^AF^BNF^XOSO_2F$, the high electronegativity of the fluorosulfate group on nitrogen mimics the electronic effects of fluorine. Thus the small $J_{AX} \simeq J_{BX}$ values of ~3.5 Hz are comparable to $^3J_{FF}$ values of 0–3 Hz in $FSO_2OCF_2NF_2$ and RCF_2NF_2 (R = F, Cl, R_f).[45] In comparison to those of FSO_2OCF_2NFX and R_fCF_2NFX (X = Cl, Br; R = CF_3, C_2F_5, F, Cl), these values imply rather different rotamer populations and (or) coupling constants of opposite sign, which average to near zero.

All the compounds reported in this work are reasonably stable at 22 °C in dry glass, with FSO_2OCF_2NBrF and C_3F_7NBrF showing some decomposition on prolonged standing at 22 °C. The reactivity of the N–Br bond was investigated with CF_3NBrF. The compound was found to be a useful reagent for thermal additions to various olefins,[46] but other obvious reactions were disappointing. On the basis of the chemistry of $(CF_3)_2NBr$,[47] we anticipated that CF_3NBrF would be an effective source of the CF_3NF· radical. However, the latter is apparently very short-lived. Both thermal and photochemical (medium-pressure Hg lamp, with and without Pyrex filter) reactions with NO and CO failed to produce $CF_3NFC(O)Br$ or CF_3NFNO in contrast to reactions of $(CF_3)_2NBr$. Similarly, under a variety of photolysis conditions no evidence was found for $(CF_3NF)_2$, an expected product on the basis of the formation of $[(CF_3)_2N]_2$ and N_2F_4 from related reactions of $(CF_3)_2NBr$ and F_2NCl,[48] respectively. Reaction of CF_3NBrF with Hg, an effective route to $[(CF_3)_2N]_2$ with $(CF_3)_2NBr$,[47] also failed to produce $(CF_3NF)_2$.

The major products in all these reactions were CF_4, N_2, and Br_2 with occasional small amounts of CF_3Br. These observations suggest that in contrast to the $(CF_3)_2N$· and NF_2· radicals, CF_3NF· is very short-lived. The radical can be effectively trapped by olefins, but in the absence of an effective trap, it decomposes to N_2 and CF_4 (eq 21).



(21)

Conclusion. The facile addition of electrophilic halogen and pseudohalogens to a perhalogenenated imine has been demonstrated with $CF_2{=}NF$ and $XOSO_2F$ (X = Cl, Br, OSO_2F). The reaction with $BrOSO_2F$ provided the first example of an *N*-bromo *N*-fluoro amine.

The oxidation of perfluoro(alkanamine) ions by halogens has also been shown to occur readily at 22 °C. The perfluoro(alkanamine) ions can be generated in situ by reaction of nitriles and imines with KF and CsF in the presence of halogens (Cl_2, Br_2). Three additional examples of *N*-bromo *N*-fluoro amines of the type R_fNBrF (R_f = CF_3, C_2F_5, C_3F_7) were obtained, and potentially useful methods were found for the synthesis of the known compounds R_fNCl_2, $R_fN{=}NR_f$, and $CF_3CF{=}NBr$ (R_f = CF_3, C_2F_5).

Acknowledgment. The financial support of this research by the U.S. Army Research Office (Grant No. DAAG29-80-C-0107) is gratefully acknowledged. D.D.D. also acknowledges the Alexander von Humboldt Stiftung for a fellowship during part of this work.

Registry No. $BrOSO_2F$, 13997-93-8; $ClOSO_2F$, 13997-90-5; $S_2O_6F_2$, 13709-32-5; $CF_2{=}NF$, 338-66-9; $FSO_2OCF_2N(F)OSO_2F$, 83949-12-6; FSO_2OCF_2NClF, 83949-13-7; FSO_2OCF_2NBrF, 83949-14-8; CF_3NCl, 13880-72-3; $FSO_2OCF_2NF_2$, 83949-15-9; CF_3OSO_2F, 926-08-9; $CF_2(OSO_2F)_2$, 6123-47-3; $CF_3CF_2CF{=}NF$, 78343-32-5; CF_3CN, 353-85-5; ClCN, 506-77-4; BrCN, 506-68-3; KF, 7789-23-3; CsF, 13400-13-0; CF_3NBrF, 82241-76-7; $CF_3NFCF{=}NF$, 41409-49-8; C_2F_5NBrF, 83949-16-0; CF_3NF_2, 335-01-3; C_3F_7NBrF, 83949-17-1; $C_2F_5NCl_2$, 677-66-7; $C_2F_5N{=}NC_2F_5$, 756-00-3; $CF_3CF{=}NBr$, 758-34-9; CF_3NCl_2, 13880-73-4; $CF_3N{=}NCF_3$, 372-63-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; CF_3OF, 373-91-1; $FOSO_2F$, 13536-85-1.

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(43) The decomposition of R_fNCl_2 to $R_fN{=}NR_f$ by both photochemical and thermal means,[3,7] as well as by reaction with Hg,[22] is known. Similarly, attempts to synthesize various R_fNBrCl derivatives result in high yields of $R_fN{=}NR_f$. (Zheng, Y.; DesMarteau, D. D., to be submitted for publication.)

(44) DesMarteau, D. D.; Hammaker, R. M.; Chang, S. C., to be submitted for publication (a vibrational assignment of CF_3NFX (X = Cl, Br, H)).

(45) Brey, W. S.; Hynes, J. B. *Fluorine Chem. Rev.* **1968**, *2*, 111.

(46) Chang, S. C.; DesMarteau, D. D. *J. Org. Chem.*, in press (additions of CF_3NBrF to C_2F_4, C_2F_3Cl, C_2H_4, $CF_2{=}CCl_2$, $CF_2{=}CBr_2$, and $CF_2{=}CH_2$).

(47) Ang, H. G.; Syn, Y. C. *Adv. Inorg. Chem. Radiochem.* **1974**, *16*, 1.

(48) Lawless, E. W.; Smith, I. C. "Inorganic High Energy Oxidizers"; Marcel Dekker: New York, 1968; p 78.