Reactions of *N*-Bromodifluoromethanimine[1]

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N-Bromodifluoromethanimine, CF_2=NBr, can be photolyzed in the presence of fluoroolefins CF_2=CFX to yield terminal imines CF_2=NCF_2CFXBr (X = F, Br) in high yields. These terminal imines can be isomerized readily by treatment with KF or CsF to the corresponding internal isomers, CF_3N=CF(CFXBr). Photolysis of CF_2=NBr at 25 °C in the presence of carbon monoxide yields bromodifluoromethyl isocyanate, $BrCF_2N$=C=O. Pyrolysis of CF_2=NBr at 550 °C yields 1,1,4,4-tetrafluoro-2,3-diazabuta-1,3-diene, CF_2=NN=CF_2, in excellent yield. Reaction of CF_2=NBr with CF_2=NF over KF produces a linear adduct, $CF_3N(F)CF$=NBr, which can be cyclized to the isomeric *N*-bromodiaziridine, $CF_3\overline{NCF_2N}Br$, by treatment with CsF. Seven new compounds are reported with characterization by IR, NMR, mass spectra, and physical properties. Alternative and improved syntheses of three compounds are also reported.

The perfluorinated *N*-haloimines, CF_2=NX (X = F, Cl, Br), provide interesting models for structural studies and an opportunity to explore the chemistry of the imine double bond and the N–X bond in an analogous series. These small molecules contain two potential reactive sites. Depending on the nature of the halogen, the N–halo bond can be the reactive link for free-radical reactions, which preserve the difluoromethylenimine functionality. On the other hand, preferential reaction of nucleophiles, especially fluoride ion, at the difluoromethylene group generates an *N*-halo anion, CF_3NX^-, which displays a varied reactivity depending on the halogen.

The versatile behavior of CF_2=NX (X = F, Cl) in the presence of alkali metal fluorides[2-4] and the thermolysis of the N–Cl bond in the olefin addition chemistry CF_2=NCl[5] have been described. CF_2=NX (X = F, Cl) have also been the subject of several structural studies.[6-8] For some time a method for the synthesis of CF_2=NBr remained elusive because methods similar to CF_2=NF and CF_2=NCl syntheses failed to produce this analogue. Finally, an unexpected source of FCN[9] provided an opportunity to attempt the preparation of CF_2=NBr by reaction of FCN with Br_2 in the presence of alkali metal fluorides.[10] This successful reaction has been refined by utilizing a more practical, large-scale source of FCN to provide useful quantities of CF_2=NBr. Studies on the reaction chemistry of CF_2=NBr have been carried out and provide interesting comparisons with known chemistry of CF_2=NF and CF_2=NCl.

Experimental Section

General Methods. All volatile materials were handled in either a stainless-steel (type 304 or 316) or glass vacuum system equipped with stainless-steel or Teflon–glass valves, respectively. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were measured by PVT measurements, assuming ideal gas behavior. Temperatures were measured by a digital readout iron–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer with a Model 7500 data station, using a 10-cm glass cell fitted with KCl windows. ^{19}F NMR spectra were recorded on either a JEOL FX-90Q or an IBM NR200AF with $CFCl_3$ as the reference and $CDCl_3$, acetone-d_6 or benzene-d_6 as the lock solvent. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer at 70 eV for both EI and CI (CH_4). Samples were introduced by direct gas injection.

Reagents. FCN was prepared by a modification of the literature technique.[11] Cyanuric fluoride (made from cyanuric chloride by the method of Tullock and Coffman[12]) was stored in a Pyrex vessel fitted with two Teflon–glass valves and containing 1 g of NaF at 0 °C. A stream of nitrogen was passed through a flow system consisting in sequence of a $CaSO_4$ drying column, a mass flowmeter, the trimer vessel, a 3 ft × $^3/_8$ in. o.d. platinum tube heated in an electric furnace to 1100 °C, and a Pyrex trap cooled to −196 °C in a hood. The flow rate was maintained at 200–500 sccm (standard cubic centimeters per minute) for 1–2 h, and in a typical run 2–5 g of $(FCN)_3$ was consumed. The products were separated by fractionation through a series of cold traps under dynamic vacuum. A −110 °C trap retained unreacted cyanuric fluoride and cyanogen. A −125 °C trap retained FCN, and a −196 °C trap collected CF_3CN and CF_3N=CF_2. Repeated distillation was necessary to obtain pure FCN. Yields of FCN were typically 20% while CF_3CN and $(CN)_2$ comprised 20–30% of the products. The balance was unreacted cyanuric fluoride and small amounts of other unidentified products.

NOTE: Cyanogen fluoride has been shown to polymerize explosively and must be handled with extreme caution. We have not experienced any explosive behavior while handling 3–30-mmol samples in glass vacuum systems at FCN pressures of less than 1 atm.

CF_2=NF[13] was prepared by a literature method. KF and CsF were activated by fusion in a platinum crucible and grinding in a ball mill under very anhydrous conditions. Other reagents were used as received or were purified by standard procedures. As necessary, product samples were further purified by GLC using a 10-ft column packed with 15–30% Halocarbon oil on Chromosorb P.

CF_2=NBr was prepared by a modification of the procedure described earlier.[10] In a typical preparation, KF (2.0 g, 34 mmol) was placed in a 100-mL two-piece Pyrex reactor joined by an Ace-Thred connector with a Viton O-ring and fitted with a Teflon–glass valve. After the vessel was evacuated, FCN and Br_2 (10.0 mmol each) were introduced at −196 °C by vacuum transfer. The flask was warmed to 22 °C under a stream of tap water, shaken for 3 min, and cooled to −196 °C. After removal of any noncondensible gases, the volatiles were quickly transferred from the flask to the vacuum line for trap-to-trap distillation at temperatures of −70, −120, and −196 °C. CF_2=NBr and some Br_2 collected at −120 °C. The −196 °C trap retained unreacted FCN (~2 mmol, 20%), which was recycled. The −70 °C trap retained CF_3NBr_2 (1.5 mmol, 15%) and Br_2. Pure CF_2=NBr was obtained

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by treatment with excess ethylene to remove traces of Br_2. The mixture of CF_2=NBr, $C_2H_4Br_2$, and C_2H_4 was separated by trap-to-trap distillation at temperatures of −55, −120, and −196 °C. Pure CF_2=NBr (6.0 mmol, 60% yield) collected at −120 °C.

Derivatives. CF_2=NN=CF_2. CF_2=NBr (3.7 mmol) was condensed into a 10-mL Pyrex tube fitted with a Teflon–glass valve. The vessel was then connected to a 1 in. o.d. × 3 ft Pyrex tube filled with short glass tubing sections (5 mm o.d.) which was connected to vacuum through a trap cooled to −196 °C. The packed section was heated to 550 °C, and the CF_2=NBr was slowly introduced into the system at static vacuum. After 5 min, a mixture of bromine and CF_2=N-N=CF_2 was observed in the −196 °C trap. The system was then reevacuated to remove a small amount of N_2. The contents of the −196 °C trap were treated with excess ethylene at 22 °C to remove the bromine and fractionated through a series of cold traps at −50, −120, and −196 °C. Pure CF_2=NN=CF_2 (1.78 mmol, 95% yield) collected in the −120 °C trap. Spectral data were in agreement with the literature.[14]

$BrCF_2NCO$. CF_2=NBr (1.0 mmol) and CO (6.0 mmol) were added to a 100-mL Pyrex reactor equipped with a Teflon–glass valve and cooled to −196 °C. The reactor was allowed to warm to 22 °C, and the mixture was irradiated with a 250-W medium-pressure Hg lamp for 12 h. Excess CO was removed by pumping on the flask at −196 °C. Some involatile material was not further characterized. The volatile product was chromatographed on a 15% Halocarbon oil on Chromosorb P column. The pure isocyanate was isolated in 55% yield: IR (10 torr) 3717 (w), 3253 (w), 2394 (w), 2281 (vs, N=C=O), 1454 (s, N=C=O), 1155 (vs), 1119 (vs), 975 (vs), 830 (m), 656 (w), 604 (w) cm^{-1}; MS (CI), m/z 174/172 (MH^+), 154/152 ($M - F)^+$, 146/144 ($MH^+ - CO$), 131/129 ($M - NCO)^+$, 109/107 ($M - CF_2N)^+$, 92 ($M - Br)^+$; MS (EI), m/z 154/152 ($M - F)^+$, 131/129 ($M - NCO)^+$, 109/107 ($M - CF_2N)^+$, 92 ($M - Br)^+$, 81/79 (Br^+), 69 (CF_3^+); ^{19}F NMR (C_6D_6) δ −46.1 (s).

CF_2=NCF_2CF_2Br. Photolysis. Into a 100-mL Pyrex reactor fitted with a Teflon–glass valve were added CF_2=NBr (1.0 mmol) and C_2F_4 (4.0 mmol). The mixture was irradiated with a 250-W medium-pressure Hg lamp for 1 h. The product mixture was separated by trap-to-trap distillation using −85, −120, and −196 °C traps. Pure CF_2=NCF_2CF_2Br (0.8 mmol, 82% yield) collected in the −85 °C trap. Some involatiles were left in the reaction vessel, which were not identified further.

Thermolysis. With the same reactor as above, the two reactants (1.0 mmol of CF_2=NBr, 4.0 mmol of C_2F_4) were heated in a water bath at 95 °C for 8 h. The yield of CF_2=NCF_2CF_2Br was 67%. The remainder of the starting material was consumed in involatile side product formation. IR (8 torr) 1799 (C=N, vs), 1317 (vs), 1288 (s), 1243 (vs), 1179 (vs), 1110 (s), 984 (s), 905 (s), 879 (s), 807 (m), 775 (m) cm^{-1}; MS (CI, major), m/z 246/244 (MH^+, 100), 226/224 ($M - F)^+$, 181/179 ($M - CF_2N)^+$, 164 ($M - Br)^+$, 131/129 ($CF_2Br)^+$, 114 ($CF_2CF_2N)^+$; MS (EI), m/z 245/243 ($M)^+$, 226/224 ($M - F)^+$, 181/179 ($M - CF_2N)^+$, 176/174 ($M - CF_3)^+$, 164 ($M - Br)^+$, 145 ($M - BrF)^+$, 131/129 ($CF_2Br)^+$, 114 ($CF_2CF_2N^+$, 100), 100 ($CF_2CF_2)^+$, 95 ($CF_2NCF)^+$, 81/79 ($Br)^+$, 69 ($CF_3)^+$; ^{19}F NMR (C_6D_6) (F^AF^BC=$NCF_2^NCF_2^MBr$) δ −27.7 (br d, A), −43.4 (br d, B), −69.2 (m, N), −93.3 (m, M), J_{AB} = 88 Hz, $J_{AM} \simeq J_{BM} \simeq$ 2 Hz, $J_{AN} = J_{BN}$ = 11 Hz, J_{MN} = 3 Hz.

CF_2=NCF_2CFBr_2. CF_2=NBr (2.0 mmol) and CF_2=CFBr (6.0 mmol) were added to a 100-mL Pyrex reactor and irradiated with a medium-pressure Hg lamp for 3 h. The volatiles were separated through traps at −70, −120, and −196 °C. Pure CF_2=NCF_2CFBr_2 (1.3 mmol, 65% yield) was isolated in the −70 °C trap. Some involatile material remained in the reactor. IR (10 torr) 1798 (C=N, vs), 1314 (vs), 1249 (vs), 1205 (vs), 1154 (vs), 1098 (vs), 1050 (m), 991 (m), 971 (m), 871 (s), 826 (vs), 771 (s), 728 (m), 605 (w) cm^{-1}; MS (CI, major), m/z 308/306/304 (MH^+), 307/305/303 (M^+), 288/286/284 ($M - F)^+$, 266/264/262, 243/241/239 ($M - CF_2N)^+$, 226/244 ($M - Br)^+$, 204/202 ($M - BrF)^+$, 193/191/189 ($CFBr_2)^+$; MS (EI), m/z 243/241/239 ($M - CF_2N)^+$, 226/224 ($M - Br)^+$, 204/202 ($M - BrF)^+$, 193/191/189 ($CFBr_2)^+$; ^{19}F NMR (C_6D_6) (F^AF^BC=$NCF_2^NCF^MBr_2$) δ −28.2 (br d, A), −44.1 (br d, B), −73.2 (m, M), −89.4 (m, N), J_{AB} = 88 Hz, $J_{AN} = J_{BN}$ = 11 Hz, J_{MN} = 14 Hz, $J_{AM} = J_{BM}$ = 2 Hz.

CF_3N=$CFCF_2Br$ and CF_3N=$CFCFBr_2$. Exposure of CF_2=NCF_2CF_2Br and CF_2=NCF_2CFBr_2 to KF for 1 h or CsF for 15 min converted the terminal imines to the internal isomers, CF_3N=$CFCF_2Br$ and CF_3N=$CFCFBr_2$, respectively, in essentially quantitative yields.

CF_3N=$CFCF_2Br$: bp 54.2 °C; mp <−125 °C; log P (torr) = 7.1565 − (1399.8/T), ΔH_{vap} = 6.40 kcal/mol, ΔS_{vap} = 19.6 eu; IR (8 torr) 1771 (vs, C=N), 1316 (s), 1254 (vs), 1209 (vs), 1133 (m), 1105 (s), 1020 (w), 962 (s), 819 (s), 774 (m), 655 (m), 624 (m) cm^{-1}; MS (CI, major), m/z 246/244 (MH^+), 245/243 (M^+), 226/224 ($M - F)^+$, 181/179 ($C_2F_4Br)^+$, 164 ($M - Br)^+$, 131/129 ($CF_2Br)^+$, 114 ($C_2F_4N)^+$; MS (EI), m/z 245/243 ($M)^+$, 226/224 ($M - F)^+$, 181/179 ($CF_2F_4Br)^+$, 174 ($M - CF_3)^+$, 164 ($M - Br)^+$, 145 ($M - BrF)^+$, 131/129 ($CF_2Br)^+$, 119 ($C_2F_5)^+$, 114 ($C_2F_4N)^+$, 100 ($C_2F_4)^+$, 95 ($CF_3NC)^+$, 69 ($CF_3)^+$; ^{19}F NMR (C_6D_6) (CF_3^MN=$CF^ACF_2^XBr$, AM_3X_2 spin system) δ −32.1 (br d, A), −57.2 (d, M), −61.6 (m, X), J_{AM} = 10.2 Hz, J_{AX} = 7.6 Hz, $J_{MX} \leq$ 1.0 Hz.

CF_3N=$CFCFBr_2$: IR (9 torr) 1759 (vs, C=N), 1282 (vs), 1255 (vs), 1201 (vs), 1128 (s), 909 (w), 839 (w), 812 (m), 794 (s), 778 (m), 750 (w), 680 (m), 618 (m) cm^{-1}; MS (CI, major), m/z 308/306/304 ($MH)^+$, 307/305/303 ($M)^+$, 288/286/284 ($M - F)^+$, 243/241/239 ($M - CF_2N)^+$, 227/225 ($MH - Br)^+$, 226/224 ($M - Br)^+$, 207/205 ($M - BrF)^+$, 193/191/189 ($CFBr_2)^+$, 176/174 ($M - CF_2Br)^+$, 131/129 ($CF_2Br)^+$, 114 ($CF_3NCF)^+$; MS (EI), m/z 243/241/239 ($M - CF_2N)^+$, 226/224 ($M - Br)^+$, 207/205 ($M - BrF)^+$, 193/191/189 ($CFBr_2)^+$, 176/174 ($M - CF_2Br)^+$, 162/160 ($C_2F_3Br)^+$, 145 ($M - 2Br)^+$, 131/129 ($CF_2Br)^+$, 114 ($CF_3NC)^+$, 112/110 ($CFBr)^+$, 81/79 ($Br)^+$, 77 ($C_2F_2NH)^+$, 76 ($C_2F_2N)^+$, 69 ($CF_3)^+$; ^{19}F NMR (C_6D_6) (CF_3^MN=$CF^ACF^NBr_2$, AM_3N spin system) δ −30.2 (dq, A), −56.6 (d, M), −68.6 (d, N), J_{AM} = 13 Hz, J_{AN} = 24 Hz, J_{MN} = 2 Hz.

$CF_3N(F)CF$=NBr. KF (1.0 g, 17 mmol) was added to a two-piece 100-mL Pyrex reactor with an Ace-Thred connector with Viton O-ring and a Teflon–glass valve. The reactor was evacuated and cooled to −196 °C. CF_2=NF (1.0 mmol) and CF_2=NBr (2.5 mmol) were added to the reactor, allowed to warm to 22 °C, and stirred for 5 h. Vacuum fractionation of the volatiles gave a mixture of $CF_3N(F)CF$=NBr and CF_2=NBr in the −80 °C trap and CF_2=NBr in the −196 °C trap. The mixture was purified by repeated dynamic distillation through a −105 °C trap to remove the more volatile CF_2=NBr. $CF_3N(F)CF$=NBr (0.5 mmol) was isolated in 50% yield based on starting CF_2=NF. (The dimer of CF_2=NF, $CF_3N(F)CF$=NF, and CF_3NBrF were not identified as side products, although these compounds comprise likely sources of yield losses.) IR (8 torr) 1688 (C=N, vs), 1295 (vs), 1245 (vs), 1213 (vs), 1167 (vs), 994 (m), 815 (w), 711 (m) cm^{-1}; MS (CI, major), m/z 229/227 (MH^+), 228/226 (M^+), 210/208 ($MH - F)^+$, 209/207 ($M - F)^+$, 148 ($MH - Br)^+$, 127/125 ($CFNBr)^+$; MS (EI, major), m/z 228/226 ($M)^+$, 147 ($M - Br)^+$, 126/124 ($CFNBr)^+$, 81/79 (Br^+), 69 ($CF_3)^+$; ^{19}F NMR (C_6D_6) (CF_3^NN-$(F^A)CF^M$=NBr, AMN_3 spin system) δ −26.6 (dq, A), −60.8 (dq, M), −70.1 (dd, N), J_{AM} = 38.3 Hz, J_{MN} = 15.5 Hz, J_{AN} = 8.4 Hz.

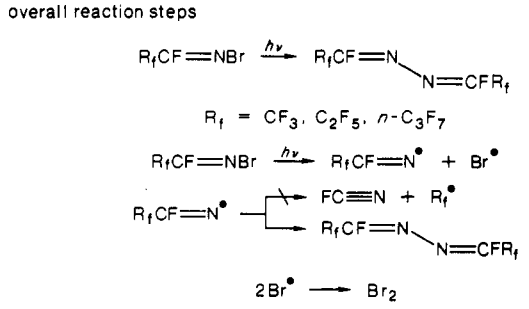
$CF_3\overline{NCF_2}NBr$. $CF_3N(F)CF$=NBr (0.5 mmol) was condensed into a 100-mL Pyrex reactor previously charged with 0.9 g (6 mmol) of CsF. After stirring for 20 min at 22 °C, the volatiles were fractionated through a −70 °C trap to remove a small amount of CF_3NBr_2. The −196 °C trap contained 0.46 mmol of $CF_3\overline{N\text{-}CF_2}NBr$ (92% yield based on starting $CF_3N(F)CF$=NBr): IR (10 torr) 1414 (s), 1382 (m), 1294 (vs), 1229 (vs), 1049 (m), 940 (m), 829 (w), 677 (m), 658 (s) cm^{-1}; MS (CI, major), m/z 229/227 ($MH)^+$, 228/226 ($M)^+$, 215, 213, 209/207 ($M - F)^+$, 149 ($M + 2H - Br)^+$, 148 ($MH - Br)^+$, 147 ($M - Br)^+$, 134 ($MH - NBr)^+$, 131/129 ($CF_2Br)^+$, 128 ($C_2F_4N_2)^+$, 114 ($C_2F_4N)^+$; MS (EI), m/z 147 ($M - Br)^+$, 131/129 ($CF_2Br)^+$, 128 ($C_2F_4N_2)^+$, 114 ($C_2F_4N)^+$, 109 ($CF_3N_2C)^+$, 95/93 ($NBr)^+$, 81/79 ($Br)^+$, 69 ($CF_3)^+$, 50 ($CF_2)^+$; ^{19}F NMR (C_6D_6) ($CF_3^A\overline{NCF^MF^NN}$-Br, A_3MN spin system) δ −64.0 (dd, A), −100.5 (br d, M), −112.9 (dq, N), J_{MN} = 32.2 Hz, J_{AN} = 11.2 Hz, J_{AM} = 2.4 Hz.

Results and Discussion

The pyrolysis of cyanuric fluoride in Pt at 1100 °C provides a simple means of obtaining useful quantities of FCN. The much more elaborate apparatus employed by

(14) Mitsch, R. A. *J. Heterocycl. Chem.* **1964**, *1*, 59.

Scheme I



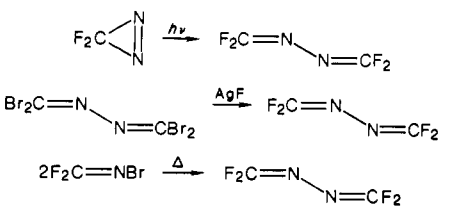
Fawcett and Lipscomb gave higher yields at an optimum temperature of ~1300 °C.[11] However, their work implies that temperatures in excess of 1200 °C are needed for good yields, thus requiring an expensive resistively heated furnace or induction heating. In our work, the 1100 °C temperature is easily obtainable with inexpensive commercial tube furnaces and the lower temperature raises the possibility of using a much less expensive material than Pt for the pyrolysis tube.

The preparation of $CF_2{=}NBr$ in small-batch reactions was greatly improved over that previously reported[10] by using short reaction times and stoichiometric amounts of Br_2. Even then, it is impossible to suppress the further oxidation of $CF_2{=}NBr$ to CF_3NBr_2, which clearly occurs at a rate comparable to that of forming $CF_2{=}NBr$:

$$FCN \xrightarrow[MF]{Br_2} CF_2{=}NBr \xrightarrow[MF]{Br_2} CF_3NBr_2$$

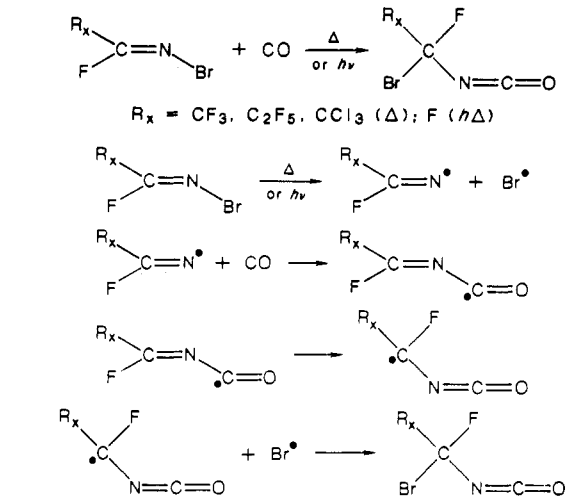
The maximum yields of $CF_2{=}NBr$ under conditions described in the Experimental Section are ~75% with an ~80% conversion of FCN to products.

In exploring the chemistry of $CF_2{=}NBr$, our interest was to compare the reactivity of the analogous series of $CF_2{=}NX$ and to compare $CF_2{=}NBr$ with other *N*-bromoimines of the type $R_fCF{=}NBr$. The thermolysis or photolysis of $CF_2{=}NF$ or $CF_2{=}NCl$ is not a practical route to the azine because of the harsh conditions necessary to cleave the N–F or N–Cl bond. Thermolysis of $R_fCF{=}NBr$ gave decomposition rather than the azines, while photolysis readily produced the respective azines as shown in Scheme I.[9] Pyrolysis of $CF_2{=}NBr$ readily produced the azine $CF_2{=}NN{=}CF_2$ in a unique reaction for the perfluoro *N*-haloiomines. This azine was first prepared by photolysis of difluorodiazirine and later by the AgF fluorination of the tetrabromo analogue $Br_2C{=}NN{=}CBr_2$.[14,15] Both prior methods are difficult to execute, and the two-step conversion from FCN to $CF_2{=}NN{=}CF_2$ is clearly superior.

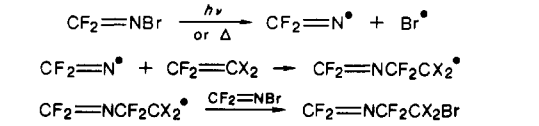


The synthesis of $BrCF_2NCO$ by the addition of CO to $CF_2{=}NBr$ is analogous to the thermal reaction of CO with other perfluoroalkyl *N*-bromoimines, which produced a series of α-bromo isocyanates.[16] Scheme II illustrates the scope of the previous reaction and includes the $CF_2{=}NBr$ example from this work. A proposed free-radical mechanism is also described.

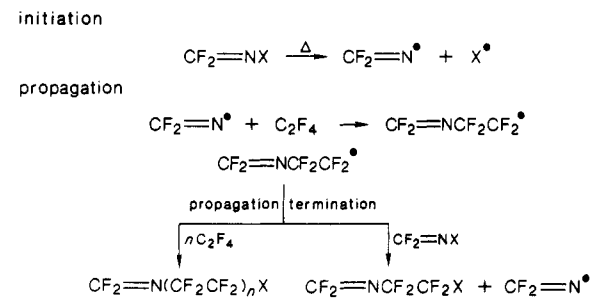
Scheme II



Scheme III



Scheme IV



Perfluoro imino radicals, $R_fCF{=}N^{\bullet}$, react with carbon monoxide differently than the saturated, bis(trifluoromethyl)aminyl, $(CF_3)_2N^{\bullet}$, which was generated from $(CF_3)_2NBr$.[17]

$$(CF_3)_2NBr + CO \xrightarrow{h\nu} (CF_3)_2NC(O)Br$$

$$CF_2{=}NBr + CO \xrightarrow{h\nu} BrCF_2N{=}C{=}O$$

The addition of $CF_2{=}NBr$ to fluorolefins of the type $CF_2{=}CFX$ (X = F, Br) occurs regiospecifically and is also best explained by a free-radical chain mechanism (see Scheme III). The best conditions for the additions consist of photolysis of a Pyrex vessel for 1–4 h or heating at 95–125 °C for 0.5–2 days. The regiospecificity of these additions are reminiscent of the earlier $CF_2{=}NCl$ additions.[5] $SF_2{=}NX$ (X = Cl, Br) exhibit similar additions to olefins.[18] For example, $SF_2{=}NBr$ adds to C_2F_4 to give both a monoadduct, $SF_2{=}NCF_2CF_2Br$ (95%), and an oligomeric product, $SF_2{=}N(CF_2)_4Br$.[18]

In comparing the olefin addition chemistry of the series of *N*-haloimines, CF_2NX (X = F, Cl, Br), a systematic

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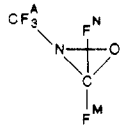
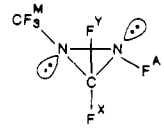
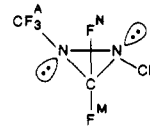
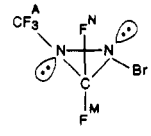
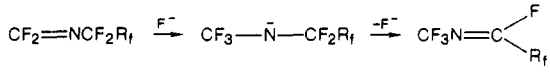
Table I

	 I	 II	 III	 IV
IR(cm^{-1})	1458	1414	1420	1410
^{19}F NMR	A −67.9	A −12.4	A −64.9	A −64.0
chemical	M −91.8	M −62.9	M −106.3	M −100.5
shifts (ppm,	N −108.1	X −111.8	N −112.4	N −112.9
rel $CFCl_3$)		Y −113.1		
coupling	J_{AM} = 3.1	$J_{AM} \leq 2$	J_{AM} = 32.5	J_{AM} = 2.4
constants	J_{MN} = 1.8	J_{AX} = 17.5	J_{AN} = 12.0	J_{AN} = 11.2
(Hz)	J_{AN} = 15.8	J_{AY} = 9.5		
		J_{XY} = 41.5	$J_{MN} = \leq 2$	J_{MN} = 32.2
		$J_{MX} \leq 2$		
		J_{MY} = 9.5		

trend in radical chain mechanism which varies with the bond strength of the initiator (in this case, the homolyzed N–X bond) is observed in the distribution of monoadduct and polymeric products. In order to propagate an olefin polymerization reaction, the initiator bond must be reasonably strong.[19] Likewise, a weak bond in the initiator will favor chain transfer after only one unit of olefin has been added. As shown in Scheme IV, the fate of the monoadduct radical is determined by the strength of the initiator bond in CF_2=NX.

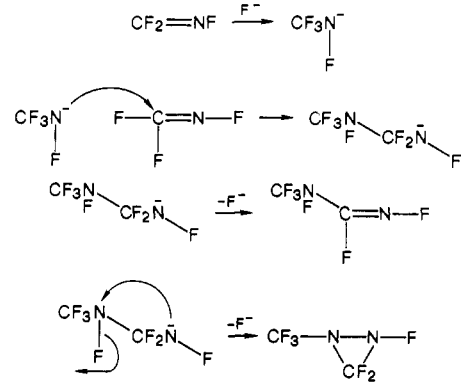
For a strong N–X bond (i.e., CF_2=NF), thermal reaction with C_2F_4 gives polymerization of the olefin with little consumption of CF_2=NF.[20] In the case of the thermal reaction of CF_2=NCl with C_2F_4, isolation of a moderate yield of the monoadduct, CF_2=NCF_2CF_2Cl, with some additional polymeric material and unreacted CF_2=NCl confirms the lower bond strength of the N–Cl compound. In this work, homolysis of the N–Br bond was achieved either by mild thermal means or brief photolysis because of a much weaker N–X bond. The major products for reactions of CF_2=NBr with olefins were monoadducts; little polymeric material was observed and no unreacted CF_2=NBr was recovered. Thus, the strength of the N–X bonds in these *N*-haloimines correspond nicely with their respective behavior in the addition to fluoroolefins. The observed regioselectivity supports the participation of a free-radical chain mechanism.

The isomerization of fluorinated terminal imines by KF or CsF has been well studied.[21,22] Quantitative yields of rearranged imines were obtained for the aforementioned adducts, CF_2=NCF_2CFBrX (X = F, Br). This fluoride-promoted isomerization or 1,3-fluoride shift is not easily reversed because of the thermodynamic stability of the internal imine.



The reaction of CF_2=NF with CF_2=NBr over active alkali metal fluorides is related mechanistically to the known dimerization of CF_2=NF over KF and CsF.[3] The proposed mechanism for the formation of the CF_2=NF dimers involves nucleophilic attack of the CF_3NF^- anion on the terminal difluoromethylene group of CF_2=NF with elimination of fluoride. Attack on the imino carbon of this linear dimer by a strong fluoride base (i.e., CsF) generates

Scheme V

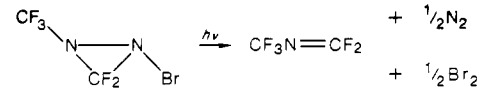


a new nitrogen anion which intramolecularly displaces fluoride from the N–F center (Scheme V).

The reaction of CF_2=NF with CF_2=NCl over CsF produced an *N*-chlorodiaziridine[5] and the availability of CF_2=NBr made the *N*-bromodiaziridine a logical target. The first attempt to combine CF_2=NF and CF_2=NBr over CsF produced only CF_3NBrF, presumably because of the decomposition of CF_2=NBr or its anion, CF_3NBr^-, in the presence of CsF and the strongly nucleophilic $Cs^+CF_3NF^-$.

The use of KF as catalyst allowed the isolation of the linear codimer $CF_3N(F)CF$=NBr. The brief exposure of this *N*-bromoimine to CsF effected the desired cyclization to the *N*-bromodiaziridine. Scheme VI depicts the proposed mechanism for the general two-step conversion of N-substituted imines to N-substituted (trifluoromethyl)-diaziridines. (The synthesis of the bis(trifluoromethyl)-diaziridine will be reported separately.[23]) Like the other *N*-halodiaziridines, the *N*-bromodiaziridine is observed only when CsF is used as the catalyst for the cyclization.

Although CF_2=NBr is only slightly sensitive to ultraviolet light, the new diaziridine contains a very reactive N–Br linkage. Exposure to Pyrex-filtered sunlight decomposed the diaziridine according to the equation shown below:



CF_3N=CF_2 is a common decomposition sink for derivatives of this ring system.[4]

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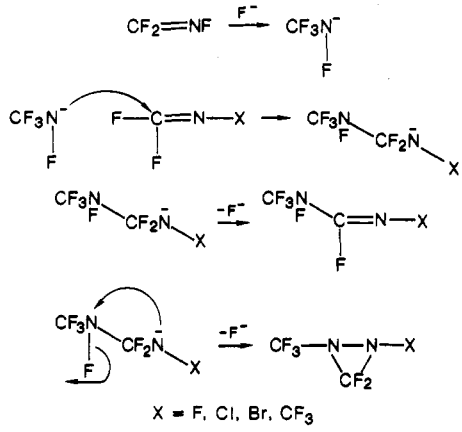
Scheme VI



A comparison of the spectral properties of the *N*-halodiaziridines prepared from CF_2=NF, CF_2=NCl, and CF_2=NBr and an analogous (trifluoromethyl)oxaziridine is provided in Table I. The characteristic ring vibration for small heterocyclic rings is observed between 1400 and 1440 cm^{-1} for each diaziridine and at 1458 cm^{-1} for the oxaziridine.[3,5,24] These frequencies are within the range expected for analogous fluorinated heterocycles.[25,26]

The ^{19}F NMR spectra are instructive regarding the probable structures of these rings. The *N*-fluorodiaziridine serves as a model from which the other structures can be reasonably assigned. As discussed in a previous report,[3] the fluorine on nitrogen provides a probe into the relative position of the other fluorines above and below the ring plane in the *N*-fluorodiaziridine. Since two distinct signals are observed for the geminal fluorines on the ring carbon, the inversion of the ring can be assumed to be slow on the NMR time scale. Likewise, the geminal fluorines are nonequivalent in the *N*-chloro- and *N*-bromodiaziridines.

Assignment of the position of the trifluoromethyl group in the N–F ring was deduced according to the relative coupling constants, since each coupling constant is measurable and distinct in this system. Close proximity in space generally renders a large coupling in rigid systems in the ^{19}F NMR.[27] According to this tenet, the trifluoromethyl group and the ring N–F were assigned as trans.[3] A cis orientation would show a large coupling constant, which is consistent with the coupling of the CF_3 group with the upper geminal fluorine (J_{MY} = 9.5 Hz) and the N–F with the lower geminal fluorine (J_{AX} = 17.5 Hz).

Diaziridines generally favor a trans arrangement of nitrogen substituents to alleviate repulsion of the two neighboring lone pairs.[28] Some diaziridines as well as triaziridines have been synthesized that can be isolated either as a cis isomer or as a mixture of isomers.[29,30] The NMR evidence favors a locked trans geometry for the *N*-fluorodiaziridine and it is reasonable to assume that the *N*-chloro- and *N*-bromodiaziridines have similar geometries in the absence of more definitive structure determinations.

In summary, CF_2=NBr provides many possibilities for additions in thermal and photochemical reactions as evidenced by its additions to fluoroolefins and carbon monoxide and its pyrolysis. Reaction with CF_2=NF over KF and CsF affirms the nucleophilicity of the CF_3NF^- anion on terminal difluoromethylene centers while indicating the poor nucleophilicity of the CF_3NBr^- anion. These two modes of reactivity make CF_2=NBr an attractive starting material for the synthesis of novel small molecules with potentially reactive centers.

Acknowledgment. The support of the U.S. Army Research Office and the National Science Foundation is gratefully acknowledged.

Registry No. I, 60247-20-3; II, 115031-89-5; III, 115031-90-8; IV, 115031-91-9; FCN, 1495-50-7; CF_3CN, 353-85-5; $(CN)_2$, 460-19-5; CF_2=NBr, 90624-74-1; CF_2=NN=CF_2, 692-73-9; CO, 630-08-0; $BrCF_2NCO$, 115031-92-0; C_2F_4, 116-14-3; CF_2=N(CF_2)$_2$Br, 115031-93-1; CF_2=CFBr, 598-73-2; CF_2=NCF_2CFBr_2, 115031-94-2; CF_3N=$CFCF_2Br$, 115031-95-3; CF_3N=$CFCFBr_2$, 115031-96-4; CF_2=NF, 338-66-9; $CF_3N(F)CF$=NBr, 115046-73-6; CF_3N=CF_2, 371-71-1; cyanuric fluoride, 675-14-9.

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Synthesis of 7-Oxygenated Aporphine Alkaloids from a 1-Benzylideneisoquinoline Enamide

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A synthesis of 7-oxygenated aporphine alkaloids is described which proceeds from readily available benzylideneisoquinoline enamides. Photocyclization of a β-acetoxy enamide leads to a protected 7-hydroxydehydronoraporphine, which can be converted into both the *cis*- and *trans*-7-hydroxyaporphines in both the nor and parent series and also the *cis*-7-methoxyaporphines in both the nor and parent series.

The aporphine alkaloids constitute a large family of benzylisoquinoline-derived alkaloids with over 300 variations isolated and identified from natural sources.[1-3] In recent years, as isolation procedures have improved, new types of aporphines have been identified. These have included the dehydro- and didehydroaporphines,[3] the 7-

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