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Fluoride-Promoted Competitive Reactions of Cyanogen Fluoride, Perfluoromethanimine, and Pentafluoro-2-azapropene[1]

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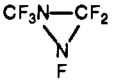
Abstract: Competitive reactions of cyanogen fluoride ($FC\equiv N$), perfluoromethanimine ($CF_2{=}NF$), and pentafluoro-2-azapropene ($CF_3N{=}CF_2$) were performed by combining pairs of the substrates over KF or CsF. These reactions establish the order of reactivity with fluoride ion as $CF_2{=}NF > CF_3N{=}CF_2 \gg F{-}C\equiv N$. Subsequent reactions of the addition products with fluoride ion, ClF, and Br_2/CsF are discussed. Seven new compounds, including a novel diaziridine, were characterized by IR, NMR, MS, and physical properties.

Fluoride-promoted reactions of fluorinated nitriles and imines have produced a number of interesting classes of compounds.[2-5] Implicit to the mechanism of these reactions is the presence of an intermediate nitrogen-based anion that can be easily oxidized by halogens and can serve as a reactive nucleophile in some cases. Perfluoromethanimine, $CF_2{=}NF$, readily forms a nucleophilic anion, CF_3NF^-, in the presence of KF or CsF.[4] Different dimers of $CF_2{=}NF$ are formed, $CF_3NFCF{=}NF$ or

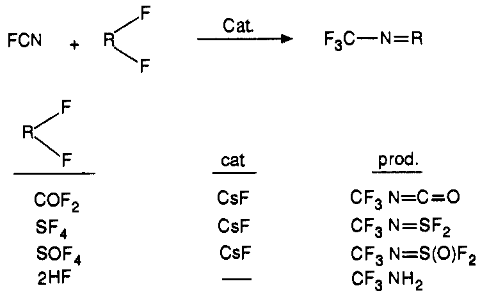


depending on the choice of alkali metal fluoride catalyst. The anion, CF_3NF^-, can also be oxidized by bromine to CF_3NBrF.[6] On the other hand, trifluoroacetonitrile is much less reactive with fluoride ion. The resultant anion, $CF_3CF{=}N^-$, is unreactive in a nucleophilic sense but is easily oxidized by bromine to the corresponding *N*-bromimine.[7] In order to study the competitive reactivity of some simple fluorinated nitrogen anions, we have chosen FCN, $CF_2{=}NF$, and $CF_3N{=}CF_2$ as substrates for alkali metal fluoride promoted reactions.

Although cyanogen fluoride has been known for over 50 years, its reaction chemistry has been limited by its availability and its explosive behavior, especially in the liquid phase.[8] Schachner and Sundermeyer have reported some reactions of FCN with CsF as a catalyst.[5] Scheme I summarizes the previous work on FCN.

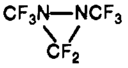
Perfluoromethanimine was studied extensively by Chang and DesMarteau.[4,6] The intermediacy of a nucleophilic anion, CF_3NF^-, has been inferred in KF- and CsF-promoted reactions of $CF_2{=}NF$.[4] The facile dimerization and other reactions of pentafluoro-2-azapropene, $CF_3N{=}CF_2$, with KF and CsF substantiate intermediacy of the reactive anion, $(CF_3)_2N^-$.[3,9] However, none of the studies have provided a basis for determining the relative reactivities of these substrates with fluoride ion. Furthermore, no estimation of the relative nucleophilicities of these reactive anions has been obtained.

Scheme I



	cat	prod.
COF_2	CsF	$CF_3N{=}C{=}O$
SF_4	CsF	$CF_3N{=}SF_2$
SOF_4	CsF	$CF_3N{=}S(O)F_2$
2HF	—	CF_3NH_2

In this work, a relative order of reactivity of these substrates with fluoride ion is established by competitive reactions. In addition, the order of nucleophilicity of the respective nitrogen anions can be determined from the relative product distribution. The competitive reactions produce two perfluorinated *N*-cyano compounds, CF_3NFCN and $(CF_3)_2NCN$, a substituted imine adduct, $CF_3NFCF{=}NCF_3$, and a symmetrical *N,N'*-bis(trifluoromethyl)diaziridine



Some derivatization of the *N*-cyano compounds to *N,N*-dichloramines, $(CF_3)_2NCF_2NCl_2$ and $CF_3NFCF_2NCl_2$, *N*-bromimine, $(CF_3)_2NCF{=}NBr$, and an *N,N*-difluoramine, $(CF_3)_2NCF_2NF_2$, was accomplished by reactions with ClF, Br_2/CsF, and F_2/CsF.

Experimental Section

General Methods. All volatile materials were handled in either a stainless steel (Type 304 or 316) or a 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, with a 10-cm glass cell fitted with KCl windows. ^{19}F spectra were recorded either on a JEOL FX-90Q or on 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 EI and CI (CH_4). Samples were introduced by direct gas injection.

Reagents. FCN was prepared by a modification of the literature technique.[8] Cyanuric fluoride (made from cyanuric chloride by the method of Tullock and Coffman[10]) was contained 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, a 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 cm^3 min for 1–2 h in a typical run, and 2–5 g of $(FCN)_3$ was consumed. The products were separated by fractionation

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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.

Caution: 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.

Fluorine was obtained from Air Products and Chemicals, Inc., and was passed through a NaF scrubber before use. ClF was made by combining equimolar amounts of Cl_2 and F_2 (0.1 mol) in a Monel cylinder (150 mL) and heating the cylinder at 230 °C for 18 h. (*Caution*: This reaction proceeds via a contained explosion, occurring at ~120 °C.) Pure ClF was removed as a gas from the cylinder at −111 °C.

$CF_2{=}NF$ and $CF_3N{=}CF_2$ were synthesized by literature methods.[11,12] 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 with a 10-ft column packed with 15–30% halocarbon oil on Chromasorb-P.

General Procedure for Competitive Reactions. All competitive reactions involving pairs of the imines or nitriles were carried out in two-piece 100-mL Pyrex reactors fitted with a Teflon-glass valve, joined by Ace-Thred connectors with Viton O-rings, and containing a magnetic stirring bar. In a typical reaction, 1 g of KF (~17 mmol) was added to the reactor in a drybox. The reactor was evacuated and cooled to −196 °C before the two reactants were introduced in equimolar amounts (1–3 mmol each) by vacuum transfer. After the mixture warmed from −196 to +22 °C, it was allowed to stir for 12 h before the volatiles were removed and separated by trap-to-trap distillation and further purified by GLC as needed.

Preparation and Characterization of the Competitive Reaction Products. $(CF_3)_2NC{\equiv}N$. On a 3-mmol scale for FCN and $CF_3N{=}CF_2$ with 17 mmol of KF as a catalyst, $(CF_3)_2NCN$ was obtained in 70% yield. The remainder of the product was the dimer of the azapropene, $(CF_3)_2NCF{=}NCF_3$ (26%), which could be separated by trap-to-trap distillation from the major product. The dimer collects at −70 °C, and $(CF_3)_2NCN$ collects at −110 °C. See ref 5 and 15 for previous spectral data. Data: IR (8 Torr) 2270 (w), 1367 (vs), 1278 (vs), 1238 (vs), 1188 (m), 1159 (m), 947 (s), 730 (m) cm^{-1}; ^{19}F NMR (C_6D_6) $\delta(CF_3) = -58.2$ (s).

$CF_3N(F)C{\equiv}N$. A 60% yield was obtained for 2.3 mmol of $CF_2{=}NF$ and 2.4 mmol of FCN over 17 mmol of KF with 0.2 mmol of $(CF_3)_2NCN$ as the only side product. $(CF_3)_2NCN$ was retained in a −110 °C trap, $CF_3N(F)CN$ was retained in a −125 °C trap, and some unreacted $CF_2{=}NF$ (0.6 mmol) was recovered in a ~196 °C trap. Data: bp −18.2 °C: mp < −155 °C; log *P* (Torr) = 7.477 − (1171.7/*T*): $\Delta H_{vap} = 5.36$ kcal/mol; $\Delta S_{vap} = 21.0$ eu; IR (10 Torr) 2243 (w), 1389 (w), 1295 (vs), 1246 (vs), 1089 (m), 984 (m), 788 (w), 674 (w) cm^{-1}; ^{19}F NMR (C_6D_6) $(CF_3{}^MN(F^A)CN$, AM_3 spin system) δ −52.2 (q, A), −71.9 (d, M), $J_{AM} = 18.3$ Hz; MS (CI) *m/z* 129 (MH^+, 100%), 128 (M^+), 109 $(M - F)^+$, 91 ($MH^+ - 2$ F), 90 $(M - 2\ F)^+$, 69 $(CF_3)^+$; MS (EI) *m/z* 128 (M^+), 109 $(M - F)^+$, 97 $(M - CF)^+$, 90 $(M - 2\ F)^+$, 83 $(CF_3N)^+$, 69 (CF_3^+, 100%).

$CF_3N(F)CF{=}NCF_3$ and $CF_3\overline{NCF_2N}CF_3$. By the reaction of 3.4 mmol of $CF_3N{=}CF_2$ and 3.4 mmol of $CF_2{=}NF$ over 17 mmol of KF, the two isomers were obtained in 95% overall yield. Fractional distillation of the volatile products after 5-h reaction time yielded 1.8 mmol of $CF_3N(F)CF{=}NCF_3$ (40%) in the −82 °C trap and 1.3 mmol of $CF_3\overline{NCF_2N}CF_3$ (55%) in the −130 °C trap. The −196 °C trap contained 0.4 mmol of unidentified products of lower molecular weight. (Although repetition of these reaction conditions produced comparable overall yields, the relative yield of diaziridine increased to as high as 72%, depending on the specific history of the KF sample employed.)

$CF_3N(F)CF{=}NCF_3$: bp 31.8 °C; mp < −125 °C; log *P* (Torr) = 8.011 − (1663.0/*T*) − (30078/T^2); $\Delta H_{vap} = 6.71$ kcal/mol; $\Delta S_{vap} = 22.0$ eu; IR (9 Torr) 1763 (vs, C=N), 1391 (s), 1325 (vs), 1268 (vs), 1219 (vs), 1074 (m), 1023 (m), 1001 (s), 867 (w), 839 (m), 747 (w), 685 (m), 655 (w) cm^{-1}; MS (CI, major) *m/z* 217 (MH^+), 216 (M^+), 198 (MH^+ − F), 197 $(M - F)^+$, 179 ($MH^+ - 2$ F), 178 $(M - 2\ F)^+$, 159 $(M - 3\ F)^+$, 129, 128, 114, 109, 85 $(CF_3CN)^+$, 69 $(CF_3)^+$; MS (EI) *m/z* 216 (M^+), 197 $(M - F)^+$, 178 $(M - 2\ F)^+$, 159 $(M - 3\ F)^+$, 128 $(NCFNCF_3)^+$, 114 $(CFNCF_3)^+$, 109, 69 (CF_3^+, 100%); ^{19}F NMR $(CF_3{}^MN(F^A)CF^Y{=}NCF_3{}^X$, AM_3X_3Y spin system) δ −35.7 (d, q, q, A), −54.8 (d, M), −68.0 (d, d, m, X), −70.5 (d, q, m, Y), $J_{AM} = J_{XY} = J_{MY} = 12$ Hz, $J_{AY} = 52$ Hz, $J_{AX} = J_{MX} \leq 2$ Hz.

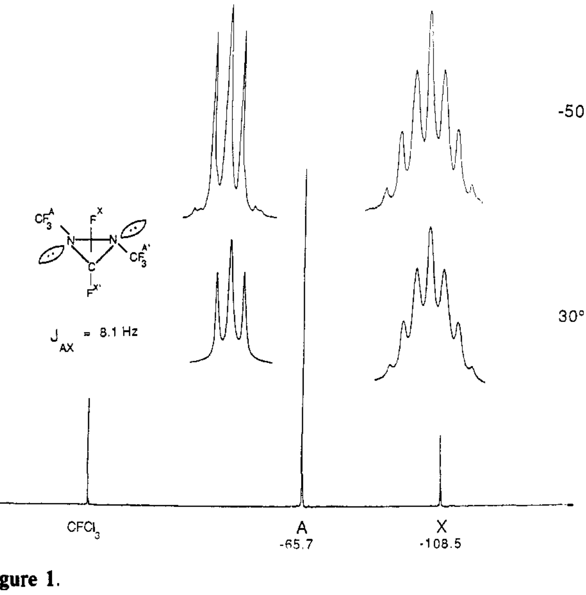

Figure 1.

$CF_3\overline{NCF_2N}CF_3$: bp −0.2 °C; mp < −155 °C; log *P* (Torr) = 8.972 − (1984.0/*T*) − (87 743/T^2); $\Delta H_{vap} = 6.14$ kcal/mol; $\Delta S_{vap} = 22.4$ eu; IR (2 Torr) 1443 (s), 1318 (s), 1279 (s), 1246 (vs), 1206 (vs), 1115 (w), 997 (m), 846 (w), 680 (m) cm^{-1}; MS (CI, major) *m/z* 217 (MH^+), 216 $(M)^+$, 198 (MH^+ − F), 197 $(M - F)^+$, 167 ($MH^+ - CF_2$), 166 $(M - CF_2)^+$, 150, 147 $(M - CF_3)^+$, 129, 128, 114 $(C_2F_4N)^+$, 109, 69 $(CF_3)^+$; MS (EI) *m/z* 216 (M^+), 128, 114 $(C_2F_4N)^+$, 109, 69 $(CF_3)^+$; ^{19}F NMR (A_6X_2 spin systems) δ_A −65.7 (t, CF_3), δ_X −108.6 (sept, CF_2), $J_{AX} = 8.1$ Hz (see Figure 1 for NMR spectra, 30 and −50 °C).

General Procedure for *N*,*N*-Dichloramine Syntheses. The nitriles were condensed into a 20-mL FEP tube fitted with a stainless steel valve. ClF was added in slight excess of a 2:1 molar ratio, and the mixture was allowed to warm from −196 to +25 °C in a cool Dewar flask. The volatiles were transferred to the glass fractionation train where excess ClF was separated from the dichloramines.

$(CF_3)_2NCF_2NCl_2$. An 81% yield was obtained from 1.0 mmol of $(CF_3)_2NCN$. The dichloramine was collected in a −110 °C trap. Data: IR (6 Torr) 1341 (vs), 1276 (s), 1225 (vs), 1192 (s), 1121 (s), 993 (vs), 971 (vs), 831 (w), 733 (m), 682 (w), 639 (w) cm^{-1}; MS (CI) *m/z* 291/289/287 (MH^+), 271/269/267 $(M - F)^+$, 253/251 $(M - Cl)^+$, 235/233 (MH^+ − ClF), 203 ($MH^+ - NCl_2$), 202 ($M^+ - NCl_2$, 100%), 152 $(C_2F_6N)^+$, 138/136/134 $(CF_2NCl_2)^+$, 114 $(C_2F_4N)^+$; MS (EI) *m/z* 290/288/286 (M^+), 271/269/267 $(M - F)^+$, 234/232 $(M - ClF)^+$, 202 ($M^+ - NCl_2$, 100%), 138/136/134 $(CF_2NCl_2)^+$, 114 $(C_2F_4N)^+$, 69 (CF_3^+); ^{19}F NMR (C_6D_6) ($(CF_3{}^A)_2NCF_2{}^XNCl_2$, A_6X_2 spin system) δ −54.2 (t, A), −78.5 (sept, X), $J_{AX} = 12.7$ Hz.

$CF_3N(F)CF_2NCl_2$. A 41% yield was removed from 0.5 mmol of $CF_3N(F)CN$. The dichloramine was retained in a −125 °C trap. Data: IR (6 Torr) 1289 (vs), 1242 (vs), 1180 (s), 1147 (s), 1035 (m), 955 (m), 839 (w), 780 (w), 687 (m) cm^{-1}; MS (CI) *m/z* 241/239/237 (MH^+), 221/219/217 $(M - F)^+$, 203/201 (M^+ − Cl), 185/183 (MH^+ − ClF), 184/182 $(M - ClF)^+$, 169, 156, 154, 152 ($C_2F_6N^+$), 147, 145, 138/136/134 $(CF_2NCl_2)^+$, 129, 120/118 $(CF_3NCl)^+$, 114 $(C_2F_4N)^+$, 102 $(CF_3NF)^+$; MS (EI) *m/z* 184/182 (M^+ − ClF), 153 $(CF_3NFCF_2H)^+$, 152 $(CF_3NFCF_2)^+$, 138/136/134 $(CF_2NCl_2)^+$, 120/118 $(CF_3NCl)^+$, 114 $(C_2F_4N)^+$, 101/99 $(CF_2NCl)^+$, 88/86/84 $(NCl_2)^+$, 83 $(CF_3N)^+$, 77, 69 (CF_3^+, 100%), 51/49 (NCl^+); ^{19}F NMR $(CDCl_3)$ ($CF_3{}^AN(F^M)CF_2{}^XNCl_2$, A_3MX_2 spin system) δ −69.0 (d, t, A), −83.3 (br t, q, M), −91.8 (d, q, X), $J_{AM} = 13.8$ Hz, $J_{AX} = 11.6$ Hz, $J_{MX} = 17.4$ Hz.

Other Derivatives. $(CF_3)_2NCF_2NF_2$. Into a 20-mL FEP reactor fitted with a stainless steel valve was placed 1.0 g (7.0 mmol) of CsF. $(CF_3)_2NCN$ (1.0 mmol) and F_2 (3.0 mmol) were condensed into the reactor at −196 °C. The reactor was allowed to warm to 22 °C in a cool Dewar over 6 h, and the excess F_2 (1.7 mmol) was removed by pumping out the reactor while it was cooled to −196 °C. The volatiles were then separated through traps at −110 and −196 °C. The −110 °C trap retained a mixture of $(CF_3)_2NCN$ and $(CF_3)_2NCF_2NF_2$ (~30% yield). The −196 °C volatiles contained a small amount of $(CF_3)_2NF$ and CF_3NF_2, which were identified by comparison with the known IR and ^{19}F NMR spectra.[13,14] The contents of the −110 °C trap were not separated further.

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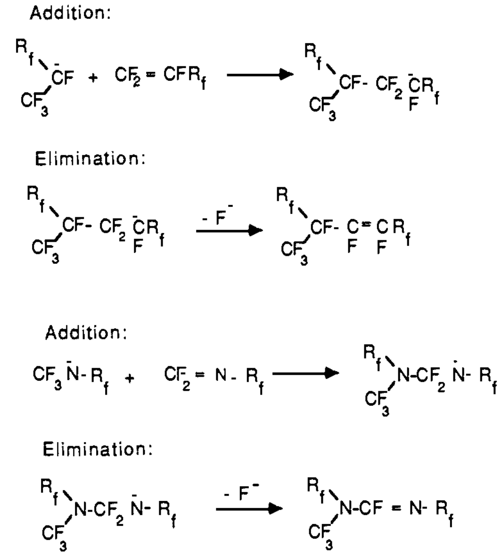
Scheme II



Data: IR (5 Torr, $(CF_3)_2NCN$ substracted) 1365 (vs), 1310 (m), 1280 (s), 1236 (vs), 1028 (m), 997 (s), 944 (m), 910 (m), 874 (w), 758 (w) cm^{-1}; ^{19}F NMR (C_6D_6) ($((CF_3^M)_2NCF_2^XNF_2^A$, $A_2M_6X_2$ spin system) δ 17.4 (br s, A), −53.7 (t, M), −115.4 (sept, X), $J_{MX} = 12.2$ Hz, $J_{AX} < 1$ Hz, $J_{AM} < 1$ Hz.

$(CF_3)_2NCF{=}NBr$. $(CF_3)_2NCN$ (2.0 mmol) was condensed into a glass reactor previously charged with 1.0 g (7.0 mmol) of CsF. Br_2 (10.0 mmol) was added, and the mixture was allowed to stand in the dark for 4–5 days. The volatiles were fractionated through a −90 °C trap to remove any unreacted $(CF_3)_2NCN$. The contents of the −90 °C trap were treated with 5.0 mmol of ethylene to remove excess Br_2. Fractionation through traps at −50 and −90 °C gave $BrCH_2CH_2Br$ and $(CF_3)_2NCF{=}NBr$ (1.8 mmol, 90% yield), respectively. Data: IR (12 Torr) 1690 (C=N, s), 1374 (vs), 1295 (s), 1274 (s), 1226 (vs), 1028 (w), 998 (m), 703 (w), 638 (w) cm^{-1}; ^{19}F NMR (C_6D_6) ($((CF_3^X)_2NCF^A{=}NBr$, AX_6 spin system) δ −9.4 (sept, A), −56.0 (d, X), $J_{AX} = 8.0$ Hz; MS (CI, major) m/z 279/277 (MH^+), 278/276 (M^+), 260/258 ($MH^+ - F$), 259/257 $(M - F)^+$, 242/240, 197 $(M - Br)^+$, 179 ($MH^+ - BrF$), 167 ($MH^+ - CFBr$), 134 $(C_2F_5NH)^+$, 127/125 $(CFNBr)^+$, 109, 107; MS (EI) m/z 278/276 (M^+), 214/212 $(M - CF_2N)^+$, 197 $(M - Br)^+$, 190/188 ($M^+ - CF_4$), 126/124 $(CFNBr)^+$, 114 $(C_2F_4N)^+$, 109 $(CF_3NCN)^+$, 81/79 (Br^+), 69 (CF_3^+).

Results and Discussion

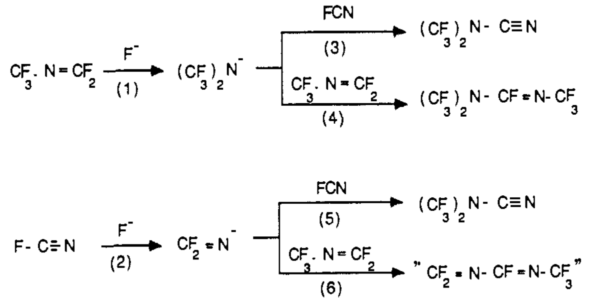
General Reactivity of Fluorinated Imines and Alkenes. Reactions of nucleophilic nitrogen-centered anions are important in the development of fluorinated nitrogen compounds. Although the carbanions derived from fluoro olefinic systems are well studied, the nitrogen analogues have received less attention despite their greater reactivity.[15] The general trend for the fluoro olefins is that less substituted olefins are more reactive. Similarly, a parallel order of reactivity for these analogous systems is shown below:

terminal imines		nitriles		internal imines
$CF_2{=}NR_f$	>	$R_fC{\equiv}N$	>	$R_fCF{=}NR_f$
terminal alkenes		alkynes		internal alkenes
$CF_2{=}CFR_f$	>	$R_fC{\equiv}CR_f$	>	$R_fFC{=}CFR_f$

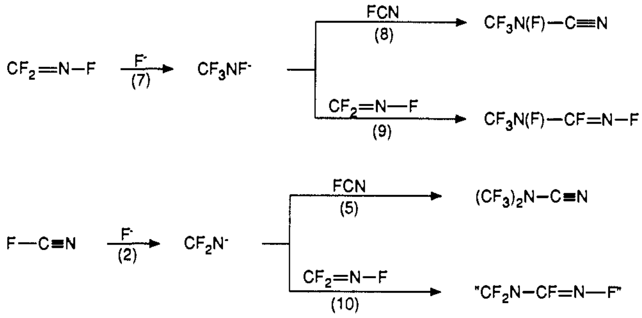
Fluoride-promoted substitution of terminal fluoro olefins gives substituted olefins by an addition–elimination sequence.[16] Suitably substituted imines and nitriles react quite readily in an analogous fashion in fluoride-promoted reactions at the imine carbon. Scheme II illustrates the addition–elimination mechanism in both systems.

In order to compare the reactivities of the anions generated by fluoride-catalyzed reactions of FCN, $CF_2{=}NF$ and $CF_3N{=}CF_2$, the substrates were combined in pairs over an alkali metal fluoride. The relevant anions in this study were therefore $CF_2{=}N^-$, $CF_3N(F)^-$, and $(CF_3)_2N^-$.

Scheme III



Scheme IV



The course of these reactions depends on the relative rates of alkali metal fluoride attack on the imines and nitrile and the relative rates of nucleophilic substitution of the anion(s) formed with the imine and/or nitrile remaining in the gas phase. A comprehensive set of possible substitution reactions is diagrammed in Scheme III for the first competitive reaction between FCN and $CF_3N{=}CF_2$.

Reactions 1 and 2 reflect the relative reactivities of the substrates with fluoride ion while reactions 3–6 relate anion nucleophilicities toward the two free substrates. Since product derived from path 6 was not observed, the contribution to the yield of $(CF_3)_2NCN$ by path 5 is probably minor as both paths are dependent upon the competitive rate of the preceding path 2. The major products arise from paths 3 and 4, which correspond in yield to 70% and 26% of the $CF_3N{=}CF_2$ initially introduced. This suggests that $(CF_3)_2N^-$ shows an ~5:1 preference for FCN over its parent imine, $CF_3N{=}CF_2$. Isolation of $(CF_3)_2NCN$ and $(CF_3)_2NCF{=}NCF_3$ as the major products establishes the superior anion formation from $CF_3N{=}CF_2$ over FCN.

The reaction of FCN with itself over KF or CsF has not been reported although fluoride-promoted addition reactions have been investigated.[5] When FCN was allowed to stand over excess KF for 2 h, the only isolated product was $(CF_3)_2NC{\equiv}N$ (approximately 80% of fluorine recovered in the product). Sundermeyer and Schachner found this compound as one of a number of products of the reaction of FCN with COF_2 over CsF.[5] Cameron and Tattershall isolated $(CF_3)_2NCN$ as the major product of the reaction of cyanogen chloride with KF.[17] Minor products included $CF_3N{=}CF_2$ and $CF_3N{=}CCl_2$. We have not isolated $CF_3N{=}CF_2$, presumably an intermediate in the conversion to $(CF_3)_2NCN$, from our reaction mixture. The increased carbon to nitrogen ratio from the reactant, FCN (1:1), to the product, $(CF_3)_2NCN$ (3:2), was noted with interest by the Tattershall group.[17] We have no further mechanistic explanation for this conversion.

In the second competitive reaction, a related set of basic reactions must be compared with the observed products. Scheme IV depicts the possibilities for the reaction of FCN and $CF_2{=}NF$ over KF. Since little $(CF_3)_2NCN$ is formed and no evidence for

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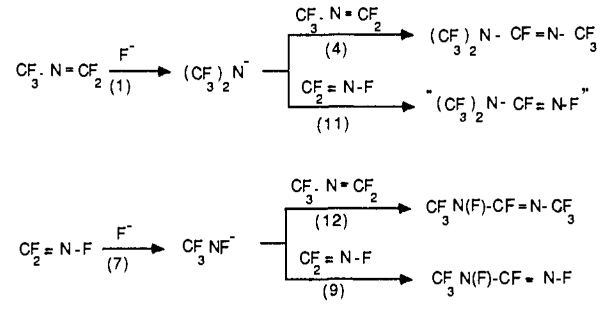
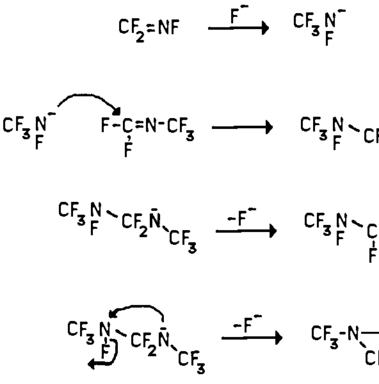
(16) See ref 15, p 104.

(17) Cameron, J. D.; Tattershall, B. W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 166.

Scheme V



Scheme VI

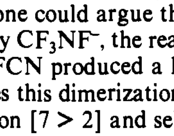


path 10 is observed, reaction 7 producing CF_3NF^- clearly predominates over reaction 2 producing $CF_2{=}N^-$. The formation of $CF_3N(F)CN$ demonstrates that the anion CF_3NF^- is formed quickly over KF and reacts selectively with FCN rather than $CF_2{=}NF$. Although one could argue that little free $CF_2{=}NF$ is available for attack by CF_3NF^-, the reaction of $CF_2{=}NF$ with KF in the absence of FCN produced a high yield of $CF_3NFCF{=}NF$.[4] Path 9 defines this dimerization path. In this reaction, selective anion formation [7 > 2] and selective nucleophilic displacement [8 > 9] generate one product, $CF_3N(F)CN$, in reasonably high yield.

An overview of the third competitive reaction between $CF_2{=}NF$ and $CF_3N{=}CF_2$ over KF is diagrammed in Scheme V. The observed products indicate that reaction 7 predominates over reaction 1 in the production of the superior nucleophile, CF_3NF^-. This nucleophile reacts selectively with $CF_3N{=}CF_2$ rather than $CF_2{=}NF$. The major products isolated from the reaction are $CF_3N(F)CF{=}NCF_3$ and the diaziridine $CF_3\overline{NCF_2N}CF_3$.

The diaziridine forms as a result of fluoride attack on the initially formed adduct and subsequent intramolecular displacement of fluoride from nitrogen as shown in Scheme VI. This rearrangement is analogous to those in related systems,[4,18-20] as shown previously for the conversion of $CF_3N(F)CF{=}NF$ to $CF_3\overline{NCF_2N}F$.[4] Brief exposure of the mixture of isomeric codimers to CsF converted all of the linear adduct to the diaziridine and provided a pure sample of diaziridine.

The structure of 1,2-bis(trifluoromethyl)-3,3-difluorodiaziridine is of interest because of its inherent symmetry. Diaziridines are known to favor a trans orientation of the nitrogen substituents in order to reduce repulsion of the two lone pairs.[21] A cis orientation of the substituents would render the methylene fluorines on the ring carbon nonequivalent. In this event, a large coupling between these fluorines should be observable in the ^{19}F NMR spectrum. The ^{19}F NMR spectrum at 20 °C shows two signals coupled by 8.1 Hz. The two CF_3 groups appear as a triplet and the CF_2 fluorines as a septet. This simple, first-order spectrum supports the trans-substituted diaziridine structure.



This structure of C_2 symmetry can be observed to be one of a pair of enantiomers when fixed in a rigid configuration. We have no reason to believe that we have enriched one enantiomer in this reaction because the reactants, $CF_2{=}NF$ and $CF_3N{=}CF_2$, are achiral with no chiral component in the reaction medium. Thus, as long as the diaziridine is locked in configuration, a racemic mixture is present.

Because of the strongly electronegative CF_3 substituents on the ring, nitrogen inversion barriers should be unusually high for several reasons.[21] In the first place, nitrogen in a three-membered ring shows hindered inversion relative to an acyclic nitrogen. Furthermore, inclusion of a second heteroatom, nitrogen or otherwise, into a three-membered aza ring further elevates the barrier of inversion for nitrogen. The *gem*-fluorines on the ring carbon of the diaziridine comprise an electronegative substituent for both nitrogens, which hinders inversion rates both in cyclic and acyclic amines.[21,22]

A variable-temperature NMR experiment was performed in order to determine the effect of temperature on the barriers to inversion of the nitrogens in the diaziridine. Although the 30 °C spectrum had revealed fairly sharp resolution for the triplet–septet pattern, the spectrum sharpened further at −50 °C but retained the same peak shapes. See Figure 1. No further change was observed at temperatures as low as −80 °C.

Higher temperatures were explored to test the barrier of inversion since the low-temperature results strongly suggested a ring system locked belows its T_c. The NMR of the diaziridine as a neat gas was run at 30 and 100 °C in a sealed NMR tube with no internal reference. The signals appeared in the same relative position in each spectrum, but resolution was diminished so that precise couplings were not attainable.

The diaziridine shows unexpectedly high thermal stability for a strained, electronegatively substituted ring system. At low pressure in the gas phase, a sample was heated to 320 °C before decomposition was observed by formation of a film within the Pyrex reactor and disappearance of the characteristic IR spectrum of the diaziridine. The mixture of volatile products was not identified.

Heating to 100 °C with $AlCl_3$ for 8 h produced no change in the IR spectrum of the diaziridine, and no reaction was observed between the diaziridine and 100% sulfuric acid.

Derivatives of the Competitive Reaction Products. Most perhalo nitriles can be treated with chlorine monofluoride to yield *N*,*N*-dichloramines.[23,24] The addition does not stop at the *N*-chlorimine stage presumably because the rate of addition of ClF is faster for the intermediate *N*-chlorimine than for the nitrile. Thus, by a 2-fold addition were the two nitriles derivatized to *N*,*N*-dichloramines, as shown below:

$$(CF_3)_2NCN \xrightarrow{2ClF} (CF_3)_2NCF_2NCl_2$$

$$CF_3N(F)CN \xrightarrow{2ClF} CF_3N(F)CF_2NCl_2$$

The two *N*,*N*-dichloramines are not sensitive to sunlight. Reaction of $(CF_3)_2NCF_2NCl_2$ with CsF and Br_2 did not product an *N*-bromo compound as was observed earlier in the conversion of CF_3NCl_2 to CF_3NBrCl and CF_3NBr_2.[25]

The reaction of perhalo nitriles with CsF and Br_2 is a demonstrated method for synthesizing *N*-bromimines.[7] The reaction

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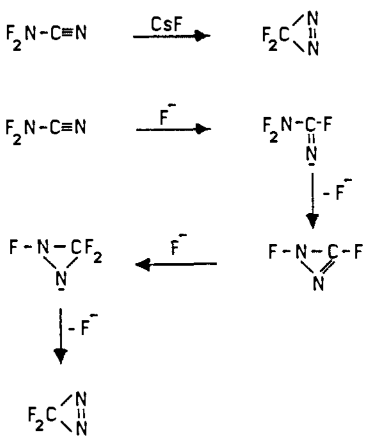
Scheme VII



of $(CF_3)_2NC{\equiv}N$ with CsF and Br_2 provides $(CF_3)_2NCF{=}NBr$. Further oxidation of *N*-bromimines to the *N*,*N*-dibromamines has been reported for some substituted nitriles,[25,26] but $(CF_3)_2NCF{=}NBr$ was not oxidized further. The steric influence of the $(CF_3)_2N$ group may prevent the attack of the fluoride base on the imine carbon. Exhaustive addition of fluorine to $(CF_3)_2NC{\equiv}N$ was accomplished by reaction with CsF and F_2, but only in conjunction with a side reaction that severed the N–CN bond. The observed product mixture for this reaction is shown below:

$$(CF_3)_2NCN \xrightarrow[F_2]{CsF} (CF_3)_2NCF_2NF_2 + (CF_3)_2NF + CF_3NF_2$$

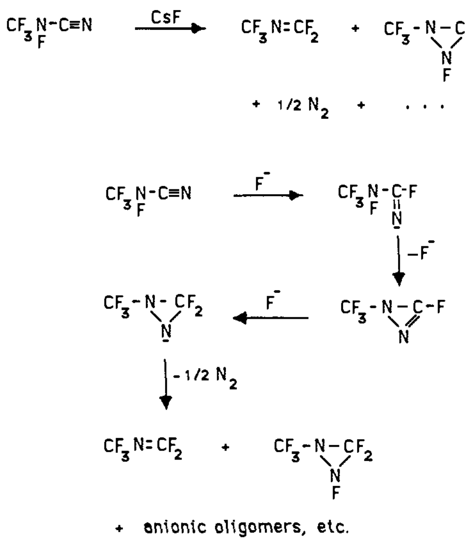
Decomposition of $CF_3N(F)CN$ over CsF. The CsF-promoted isomerization of difluorocyanamide, $F_2NC{\equiv}N$, led to the diaziridine, $\overline{CF_2N{=}N}$.[19,20] Scheme VII illustrates the proposed mechanism, which invokes fluoride attack on the nitrile carbon to produce a nitrogen anion. This anion undergoes an intramolecular nucleophilic attack on the NF_2 group to yield a 2-diazirine that rearranges to the more stable 1-diazirine by successive gain and loss of a fluoride ion.

The reaction of $CF_3N(F)C{\equiv}N$ with CsF bears a similarity to that of $NF_2C{\equiv}N$. The anticipated pathways in this reaction are shown in Scheme VIII. Attempts to pump off the intermediate diazirine were unsuccessful. Among the volatile products of the reaction were $CF_3N{=}CF_2$, nitrogen, and *N*-fluorodiaziridine ($CF_2{=}NF$ dimer). The remaining cesium salts displayed a bright yellow color, which indicated that some material remained behind as salts or oligomeric byproducts. The reactive intermediate diazirine shown in Scheme VIII may absorb fluoride ion to produce a diaziridine anion. Our failure to isolate the intermediate diazirine speaks for the apparent instability of the diaziridine anion. A related azirine, $CF_3\overline{CF{-}CF{=}N}$, was reported by Krespan to polymerize in the presence of fluoride ion.[27] Ths azirine is unstable but decomposes without loss of nitrogen. The mechanism of the decomposition of $CF_3N(F)CN$ is clearly not a simple, uniform process. Several pathways may lead to the consumption of the *N*-cyanoamine, not all of which involve the diaziridine anion as the final intermediate.

Competitive Reactions of Nitrogen-Based Anions. Several considerations are significant in determining the usefulness of fluoride-promoted competitive reactions of nitrogen-based anion. One important limitation is the favored dimerization of fluorinated terminal imines. $CF_2{=}NF$ and $CF_3N{=}CF_2$ represent not only two of the most desirable anion sources but also two of the most easily dimerized imines. In order to gain advantage from competitive reactions, attack by the desired nitrogen anion on the coreactant imine must predominate over the pathways leading to dimerization and side products.

For general use with difluoromethylenimino systems, the nucleophilic attack of a nitrogen anion on the imine carbon is the critical step. Unfortunately, a competitive side reaction for many terminal imines is conversion to a much less reactive internal aimine by successive gain and loss of fluoride ion. In fact, only terminal imines lacking a fluorine on the α-carbon are completely exempt from this limitation. The sole exception is $CF_3N{=}CF_2$, which undergoes a degenerate fluoride ion isomerization, thereby maintaining its integrity as a terminal imine. This unique isomerization is illustrated below:

Scheme VIII



$$CF_2{=}NCF_3 \underset{}{\overset{F^-}{\rightleftharpoons}} (CF_3)_2N^- \overset{-F^-}{\rightleftharpoons} CF_3N{=}CF_2$$

As has been found in this study, the observed order of anion reactivity for these three substrates is

$$CF_3NF^- > (CF_3)_2N^- \gg CF_2{=}N^-$$

The nucleophilic anions, CF_3NF^- and $(CF_3)_2N^-$, display differing selectivities in attacking neutral substrates. While CF_3NF^- attacks FCN or $CF_3N{=}CF_2$ preferentially over $CF_2{=}NF$, $(CF_3)_2N^-$ selects FCN over its parent imine, $CF_3N{=}CF_2$, in a ~5:1 ratio. These results are consistent with previous studies of CF_3NF^- with acyl fluorides[4] and studies of SF_5NF^- with acyl fluorides and $CF_2{=}NF$, in which SF_5NF^- was even more reactive than CF_3NF^-.[28]

An imine candidate for fluoride-promoted competitive reactions must possess reactive acyl-type fluorines that can be displaced by an active nucleophile. Terminal imines are sufficiently reactive with nucleophiles, as long as they are not readily rearranged by fluoride. For a viable terminal imine system, $CF_2{=}N{=}R_f$, the expected reactions with each of the substrates of this study are shown below.

$$CF_3NF^- + CF_2{=}NR_x \xrightarrow{-F^-} CF_3NFCF{=}NR_x$$

$$(CF_3)_2N^- + CF_2{=}NR_x \xrightarrow{-F^-} (CF_3)_2NCF{=}NR_x$$

$$CF_3N^-R_x + FCN \xrightarrow{-F^-} R_xN(CF_3)CN$$

The two reactions with $CF_2{=}NF$ and $CF_3N{=}CF_2$ involve simple displacements of fluoride from the terminus of the less reactive imine by the strong nucleophiles CF_3NF^- and $(CF_3)_2N^-$. In the third example, the anion generated by the competing imine should serve as a nucleophile in displacing fluoride ion from FCN.

Reactions of competing imines can be utilized for intermolecular additions if the nitrogen anion of the one component is nucleophilic enough to displace fluoride from the other substrate. The coreactant must contain an electrophilic center that will not undergo a facile fluoride 1,3-shift under the reaction conditions. The nucleophiles that have demonstrated their efficiency in this mode

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of reaction are CF_3NF^- and $(CF_3)_2N^-$. $CF_2{=}N^-$ is consistently defeated as a nucleophile, but FCN can be used as an electrophilic substrate with a suitably nucleophilic anion. The list of imines that have been successfully attacked by CF_3NF^- includes the $CF_2{=}NX$ series (X = F, Cl, Br)[4,18,29] and $CF_3N{=}CF_2$, but other qualified substrate imines should behave similarly.

Alkali metal fluoride promoted reactions of the other *N*-halodifluoromethylenimines, $CF_2{=}NX$ (X = Cl, Br), offer little evidence of nucleophilic anions like CF_3NF^-. Neither the CF_3NCl^- anion near the CF_3NBr^- anion, both far less stable over the metal fluoride surface, have reacted nucleophilically with any of the substrates that we have examined.[18]

In summary, the competitive reactions of the perfluorinated imines, $CF_2{=}NF$ and $CF_3N{=}CF_2$, and FCN in the presence of KF and CsF generate new compounds that include fluorinated *N*-cyano compounds and a stable symmetric diaziridine. These reactions establish a relative order of reactivity for these substrates with alkali metal fluoride and the corresponding order of nucleophilicity for the related anions. Some derivatives of the *N*-cyano compounds, including two *N*,*N*-dichloramines and an *N*-bromimine, have been synthesized.

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

Registry No. FCN, 1495-50-7; $CF_3N{=}CF_2$, 371-71-1; $(CF_3)_2NCN$, 54657-79-3; $(CF_3)_2NCF{=}NCF_3$, 686-39-5; $CF_3\overline{NCF_2N}CF_3$, 123837-30-9; $CF_3N(F)CF{=}NCF_3$, 666-95-5; $(CF_3)_2NCF_2NCl_2$, 123837-31-0; $CF_3N(F)CF_2NCl_2$, 123837-32-1; $(CF_3)_2NCF_2NF_2$, 123837-33-2; $(CF_3)_2NCF{=}NBr$, 123837-34-3; $CF_2{=}NF$, 338-66-9; $CF_3N(F)CN$, 123837-35-4.

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The Mechanism of Formation of *m*-Xylylene Type Biradicals Produced by Photolysis of Polymethyl Benzenes or Dihalomethyl Benzenes

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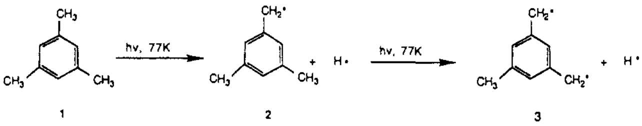
Abstract: The mechanism of formation of the mesitylylene biradical (**3**) produced by short-wavelength photolysis of matrix-isolated mesitylene (**1**) has been investigated. The data rule out a mechanism involving the sequential formation of the biradical **3** via photolysis of the *m*-methylbenzyl radical **2**. The data are most consistent with a mechanism in which the nascent H atom formed by initial scission of a benzylic carbon-hydrogen bond partitions between reaction with the matrix (MH) and abstraction from the *m*-methylbenzyl radical (**2**). The monoradical is produced by photolysis of the triplet state of mesitylene with 249-, 337-, or 405-nm excitation. Laser-induced fluorescence (LIF) experiments using a dihalide precursor produces the emission spectrum of *m*-xylylene. This is the first ambient temperature spectroscopic detection of *m*-xylylene.

The short-wavelength photolysis of matrix-isolated *m*-dimethylbenzene derivatives produces a mixture of persistent mono- and biradicals. These fragments are produced by the dissociation of the C–H bonds of one or two methyl groups of the parent molecule. Both the mono- and biradicals have been detected by their fluorescence spectra in a rigid matrix.[1]

Several years ago, Albrecht and co-workers[2] studied the photochemically induced benzyl C–H bond scission reactions of durene, which produced the duryl monoradical. Upon studying the yield of duryl radical as a function of the radiation intensity, it was concluded that the formation of duryl radical changed from a two-photon to a one-photon process upon raising the photon energy from 4.51 eV (275 nm) to 4.66 eV (252 nm). Such studies have never been extended to the biradicals produced from methylated benzenes, where the key mechanistic question is whether the biradical is formed directly from the parent molecule or by a stepwise mechanism involving secondary photolysis of a *m*-methylbenzyl monoradical.

The aim of the present work is to determine the mechanism of formation of *m*-xylylene type biradicals. We have recently reported[3] that *m*-xylylene can be prepared by photolysis of α,α′-dichloro-*m*-xylene in addition to the original aromatic hydrocarbon precursor. Our previous studies have shown that the biradical derived from mesitylene (1,3,5-trimethylbenzene) is more easily detected than that derived from *m*-xylene. Herein we propose an explanation of this observation and a mechanism for the formation of *m*-xylylene type biradicals produced by photolysis of matrix-isolated mesitylene and α,α′-dichloro-*m*-xylene.

Scheme I



Results and Discussion

Methylbenzene Precursors. The 254-nm photolysis of mesitylene in low-temperature matrices (77 K) produces 3,5-dimethylbenzyl monoradical and the mesitylylene (3-methyl-*m*-xylylene) biradical whose fluorescence spectra originate around 487 and 452 nm, respectively. Since both species are always

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[†] The Ohio State University.

[‡] CNRS.

[1] Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

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