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CESIUM FLUORIDE-ASSISTED REACTIONS OF SYN AND ANTI N-FLUORO-1-CYANO-1-FLUOROMETHANIMINE WITH CHLORINE AND BROMINE [1]

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SUMMARY

The CsF-assisted reactions of **syn** and **anti**- NCCF=NF with Cl_2 and Br_2 and the uncatalyzed addition of ClF are described. Chlorine reacts only with the imine function, whereas Br_2 reacts with both carbon-nitrogen multiple bonds. The more reactive **syn** isomer is isomerized to the **anti**-isomer under the reaction conditions. Six new compounds are reported and their structures assigned by ^{19}F NMR and infrared spectroscopy: $Cl_2NCF_2CF_2NClF$ **I**, $NCCF_2NClF$ **II**, $NCCF_2NFBr$ **III**, **syn** - BrN=CFCF=NF **IV**, **syn** - Br-N=CFCF$_2$ NBrF **V**, and **syn** - BrN=CFCF$_2$NClF **VI**.

INTRODUCTION

The synthesis and reactivity of fluorinated imines and nitriles have been of renewed interest in the last ten years, especially concerning their oxidations with halogen fluorides and related compounds to novel N-

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halogen derivatives [2] and with peroxides to oxaziridines [3]. More recently, the fluoride-assisted bromination and chlorination of nitriles and imines has provided routes to a variety of new N-halogen compounds [4-6] and the discovery of the metal fluoride-promoted conversion of N-Cl bonds to N-Br bonds further expanded the variety of N-halogen species obtainable [7,8]. Methods are now available for the facile synthesis of $R_fCF=NX$ and R_fNXX' (X,X'=F,Cl,Br).

As an extension of this work, we wanted to investigate the reactivity of a compound containing both a C-N double and a triple bond. The candidate selected was $N\equiv CCF=NF$ [9], readily available from $CF_2=NF$ [10] as a mixture of **syn** and **anti** isomers. The reactions with Cl_2 and Br_2 in the presence of CsF and with ClF are described.

EXPERIMENTAL SECTION

General Methods. Volatile compounds were handled in a Pyrex or stainless steel (304 and 316) vacuum system equipped with a Wallace and Tiernan Series 1500 differential pressure gauge. Gaseous materials were measured with the assumption of the ideal gas law. Nonvolatile materials were weighed. ^{19}F NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 84.3 MHz. All chemical shifts are reported relative to internal CCl_3F. The usual solvent was ~80 mole % CCl_4 and ~20 mole % $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer connected to a 3600 data station. A 10-cm glass cell fitted with KCl windows was employed. Mass spectra were taken on a HP 5985-B GC/MS instrument at 15 eV for EI and 50 eV for CI (CH_4). Samples were introduced by direct gas injection. M. p. were taken using a modified Stock procedure.

Reagents. The chemicals Br_2, Cl_2, CsF, and KCN were obtained from commercial sources. The compounds $CF_2=NF$ [10], HCN [11], and NCCF=NF [9,12] 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.

Reactions. Compounds **II-VI** were prepared in 100-ml glass bulbs fitted with a glass-Teflon valve. Cesium fluoride which had been fused and ground to a fine powder in a dry box was added to the reactor in the dry box. The reactor was then evacuated, cooled to -196°C, and the gaseous reactants were added by vacuum transfer. The reactor was then allowed to warm up to an appropriate temperature for an appropriate time (Table I). After the reaction, any non-condensible gases were removed by vacuum after cooling the reactor to -196°C, and the remaining volatile materials were separated by fractional condensation through a series of cold traps. Compound **I** was prepared in a 30-ml Hoke stainless steel vessel equipped with a stainless steel valve. A stainless steel vacuum line was used for transferring the reactants ClF and NCCF=NF in a mole ratio of 3:1. The reactor was allowed to warm gradually from -196°C to -50°C over a 2 hour period. The products of the reaction were separated by fractional condensation giving ~58% compound **I** [13] and ~40% compound **II**. The reactions are summarized in Table I and the characterization of the new compounds is given below.

$Cl_2NCF^{A'}F^{B'}CF^{A}F^{B}NClF^{X}$ (I): NMR (second-order A'B'AB- type). δ -106.8 (m,A), -98.6 (m,B), -97.7 (m,A'), -92.6 (m,B'), -5.2 (br s, X); J_{AB}=195.3,

$J_{A'B'}$=180.6, J_{BX}=34.2, J_{AX}=2.3, $J_{B'X}$=14.6, $J_{A'X}$=0 Hz; IR 1293 (m), 1219 (vs), 1202 (vs), 1149 (vs), 1138 (vs), 1052 (s), 1025 (s), 927 (m), 889 (m), 786 (m), 740 (s) cm^{-1}; MS (EI), major m/z 252/254/256/258 (M^+), 184/186/188 ($Cl_2NCF_2CF_2^+$), 130/132 ($CFCFNFCl^+$), 99/101 (CF_2NCl^+), 49/51 (NCl^+).

$NCCF^AF^BNClF^X$ (II): NMR (second-order ABX-type) δ -86.5 (m,A), -82.9 (m,B), 0.99 (br s,X); J_{AB}=220, J_{AX}=14.7, J_{BX}=29.3Hz; IR 2264 (m), 1219 (vs), 1212 (vs) 1189 (s), 1184 (s), 1118 (s), 922 (m), 838 (m), 832 (m), 735 (w), 690 (w) cm^{-1}. MS (CI), major m/z 145/147 (MH^+), 125/127 ($NCCF_2NCl^+$) 118/120 (CF_2NFCl^+), 107/109 (MH^+-2F), 91 (MH^+-FCl), 76 ($NCCF_2^+$); M.p < -110°C.

$NCCF^AF^BNBrF^X$ (III): NMR (second-order ABX-type) δ -84.4 (m,A), -81.2 (m,B), -10.5 (br s,X); J_{AB}=223, J_{AX}=24.4, J_{BX}=36.6 Hz; IR 2261 (m), 1215 (s), 1202 (vs), 1177 (m), 1107 (s), 967 (w), 919 (m), 809 (w), 680 (w) cm^{-1}. MS (EI), major m/z 188/190 (M^+), 124/126 ($FCNBr^+$), 105/107 ($NCBr^+$), 90 ($NCCFNF^+$) 76 ($NCCF_2^+$).

$BrN{=}CF^MCF^A{=}NF^X$ (IV): NMR (AMX-type) δ -23.9 (d,d,M), -75.9 (d,d,A) -14.6 (br d, X); J_{MX}=5.2, J_{MA}=17.4, J_{AX}=39.6 Hz; IR 1664 (s), 1367 (m), 1240 (w), 1211 (m), 1161 (s), 979 (s), 758 (m), 735 (w), 662 (m) cm^{-1}. MS (EI), major m/z 188/190 (M^+), 174/176 ($M-N^+$), 169/171 ($M-F^+$), 109 ($M-Br^+$).

$BrN{=}CF^MCF^AF^BNBrF^X$ (V): NMR (ABMX-type) δ -96.7 (m,A), -94.1 (m,B), -20.4 (d,t,M) -16.2 (br s, X); J_{AB}=190.5, J_{AX}=19.5, J_{BX}=39.1, J_{BM}=12.2, J_{AM}=J_{MX}=6.1 Hz; IR 1690 (s), 1306 (s), 1216 (s), 1146 (s), 1080 (s), 916 (m), 742 (m), 674 (w), 658 (w), 637 (w) cm^{-1}; MS (CI) major m/z 287/289/291 (MH^+), 267/269/271 ($M-F^+$), 189/191 (MH^+-BrF), 174/176 ($BrNCFCF_2^+$), 169/171 ($BrNCFCFN^+$), 124/126 ($BrNCF^+$), 109 ($NCCF_2NF^+$), 93/95 (BrN^+); M.p -18°C.

$BrN{=}CF^MCF^AF^BNClF^X$ (VI): NMR of a mixture of **V** and **VI** gives discrete peaks for F^A, F^B, and F^X due to compound **VI**. The F^M in compound (**V**) has δ at -20.1 ppm which overlaps with the F^M in (VI) (δ = -20.4 ppm) giving rise to an octet pattern with intensity ratios 1:2:2:3:3:2:2:1, with $J_{MX} = J_{MA} = 1/2\ J_{MB} = 6.1$ Hz. Other resonances for (VI) occur at δ -100.7 (m,A), -96.8 (m,B), -6.1 (br s, X); $J_{AB} = 188.3$, $J_{AX} = 15.3$, $J_{BX} = 26.9$ Hz. The intensity of the NMR signals indicate the ratio of compounds (**VI**) to (**V**) is approximately 1. IR of the mixture is essentially the same as (**V**). MS (CI) gives a base peak corresponding to molecular ions of (**VI**) m/z 243/245/247 (MH^+), 174/176 $(BrNCFCF_2)^+$, 130/132 $(FCCF_2NCl)^+$, 124/126 $(NBrCF)^+$.

RESULTS AND DISCUSSION

Previously, NCCF=NF was shown to undergo facile nucleophilic substitution of the methylene fluorine [9]. As expected, we found no reactivity of the compound with the weak electrophiles Br_2 and Cl_2 alone. This is consistent with previous work where CF_2=NX, R_fCF=NX (X=F, Cl, Br) and R_fCN were essentially inert to Cl_2 and Br_2 [4-8,14]. In contrast, and as expected, NCCF=NF reacts readily with the more electrophilic halogen source ClF as shown (see Table 1).

$$\mathrm{NCCF{=}NF} \xrightarrow{\mathrm{ClF}} \mathrm{Cl_2NCF_2CF_2NFCl}\quad \mathbf{I} + \mathrm{NCCF_2NClF}\ \ \mathbf{II}$$

A large number of reactions of ClF with a variety of >C=N- and -C≡N compounds, as well as a number of examples with strong halogen electrophiles such as FSO_2OX (X=Cl, Br), have shown this to be a general high-yield reaction [2,4,15]. In this case, with ClF, there is an apparent differentiation in reactivity of the C=N versus the C≡N bond. This is consistent with earlier attempts by us to prepare $R_fCF=NCl$ by low-temperature reactions of ClF with excess R_fCN. The dominant reaction under all conditions tried was the formation of only $R_fCF_2NCl_2$, implying that $R_fCF=NCl$, a necessary intermediate, was more reactive than R_fCN [16].

When CsF is added to the reactions of NCCF=NF with Cl_2 and Br_2, the expected facile chloro- and bromofluorinations are observed. The starting NCCF=NF is a 95 to 5 mixture of **syn** and **anti** isomers, and during the reaction the **syn** isomer is isomerized to the **anti**-isomer as previously observed in the presence of metal fluorides [9]. Both isomers are reactive, with the **anti** isomer being somewhat less reactive. Limited reactions carried out with essentially the pure **anti** isomer appeared to be slower and gave lower yields under the same conditions than the usual 95-to-5 mixture.

A summary of typical reactions and the observed products are shown in Table 1. The low yields are due in part to the fact that both **syn**- and **anti** -NCCF=NF are absorbed by the CsF on standing to give an unknown solid (presumably a polymer) which when subsequently reacted with halogen does not give the indicated products. The observed products show that in the case of the oxidant Cl_2 only the imine function undergoes reaction, whereas Br_2 reacts with both C-N functions. This is surprising since Cl_2 is a stronger oxidant than Br_2 and one might expect the reverse. Also, we had previously shown that R_fCN was converted to $R_fCF_2NCl_2$ by Cl_2/CsF, although the reaction rate decreases with increasing size of R_f and this must be a factor here [4,17]. In our opinion, the greater reactivity of Br_2 is due to a stable complex formed by Br_2 and CsF which somehow facilitates activation of the -C≡N bond [8, 18].

TABLE 1.

Summary of Reactions of NCCF=NF

Reactants[a]	**(mmol)**	**Conditions(°C/h)**	**Products(%)[b,c,d]**
NCCF=NF	X_2		
1.5	ClF, 4.5[e]	-196 to -50°/2	$Cl_2NCF_2CF_2NClF$ **I** (58), $NCCF_2NClF$ **II** (40), other
1.0	Cl_2, 5.0	22/20	**II** (24), N_2, other
1.0	Cl_2, 1.6	-70/15	**II** (100)
1.0	Br_2, 2.3	-78 to -70/16	$NCCF_2NBrF$ **III** (20), A, other
1.0	Br_2, 2.0	-50/16	BrN=CFCF=NF **IV** (31), $BrN{=}CFCF_2NBrF$ **V** (5), A, other
1.0	Br_2, 3.0	-60 to -20/6.5	**V** (22), **IV** (4), A, other
II 0.5	Br_2, 1.3	-100 to -40/15	**V** (30), $BrN{=}CFCF_2NClF$ **VI** (30), other

[a]~ 1 to 2g CsF. [b]A = anti - NCCF = NF. [c]other = low molecular weight products not identified and unreacted X_2. [d]yield based on starting C-N compounds. [e]no CsF present.

For both Cl_2 and Br_2, the concept that the reaction with an imine function in the presence of CsF takes place by an intermediate amine ion seems valid.

$$R_fCF{=}NF + F^- \xrightarrow{CsF} R_fCF_2NF^- \xrightarrow{X_2} R_fCF_2NXF + X^-$$

For the first step in the oxidation of the nitrile, a similar sequence can be proposed, i.e.

$$R_fCN + F^- \xrightarrow{CsF} R_fCF{=}N^- \xrightarrow{X_2} R_fCF{=}NX + X^-$$

However, it is difficult to reconcile the apparent difference in reactivity of Br_2 -vs- Cl_2 for NCCF=NF if this is the only consideration.

For Br_2, the results in Table 1 do not give a clear differentiation in the relative reactivity of the double and triple bonds, but the imine function appears to be more reactive. Whereas certain nitriles are oxidized to the N,N- dibromo derivative [6,8]. these reactions are usually slow at 22°C [5] and thus no $-NBr_2$ products are observed under the conditions employed in this work. The formation of **V** in the reaction of **II** with Br_2 is clearly due to the fluoride-promoted conversion of an N-Cl bond to an N-Br bond as has been previously observed for NCl_2 species [7,8].

The structural characterization of compounds **I - VI** is straightforward from the data given in the experimental section. Intense parent ions could be observed for each compound in the EI or CI mass spectrum with the expected isotopic ratios for chlorine and bromine. The infrared spectra show characteristic ν (C≡N) for **II** and **III** at ~2260 cm^{-1} and ν (C=N) for **IV - VI** at 1660 - 1690 cm^{-1}. Strong ν (C-F) bands are seen in each compound in the 1100 - 1300 cm^{-1} region and bands for ν (N - X) are apparent for N-F (1000 - 900 cm^{-1}) and N-Cl and N-Br (800 - 650 cm^{-1}) but these frequencies cannot be readily assigned with the available data [8].

The ^{19}F NMR provides convincing proof of structure for each compound. Compounds **I** - **III** exhibit characteristic ABX patterns for the A $-CF^AF^BNXF^X$ moiety as found for many related molecules, with $J_{AB} \simeq 200$ Hz [19]. Interestingly, the fluorines of the $Cl_2NCF^{A'}F^{B'}$ - group in **I** are also diastereotopic due to the more distant chiral -NClF group, but there is essentially no ^3J coupling between A'B' and AB fluorines. Compound **IV** exhibits an AMX spin system where it can be argued that the configuration is **cis-cis**. J_{AX} is only 40 Hz and F^A must therefore be **cis** to X*. Similarly, the chemical shift of F^M at δ -24 indicates M is **cis** to Br**.

Finally, for **V** and **VI** an ABMX spin system is observed with a large J_{AB} value similar to **I** - **III** and a δ F^M = -20, indicating M is **cis** to Br.

CONCLUSION

Reactions of NCCF=NF with ClF, Cl_2/CsF and Br_2/CsF demonstrate that the imine double bond is more reactive than the nitrile triple bond, allowing selective halogenation to $NCCF_2NXF$ under mild reaction conditions. Both functions can be halogenated with ClF and Br_2/CsF with

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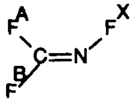
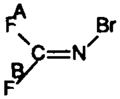
*In

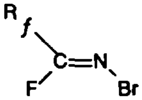


, J_{AX} = 22.1 and J_{BX} = 184 Hz. See references 9 and 12 and references therein.

**In



, δ_A = -31.3 and δ_B = -54.3 and in a variety of



δ(F) $\simeq$ -20. See references 5, 6 and 13 and references therein.

ClF converting the nitrile function to the N,N-dichloroamine and Br_2/CsF only to the N-bromoimine, whereas Cl_2/CsF was unreactive under all conditions tried with the nitrile function. Methods are now available for synthesis of a remarkable number of the possible halogenated derivatives of cyanogen of the type $XX'NCF_2CF_2NXX'$ and $X'N{=}CFCF{=}NX$ and $XN{=}CFCF_2NXX'$ (X,X'=F, Cl, Br).

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