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# Chlorofluorination of Nitriles. Preparation of *N*-Chloro-*N*-fluoroalkylamines

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The reaction of halogenated nitriles with a 1:1 mixture of $ClF-F_2$ proceeds in high yield to form *N*-chloro-*N*-fluoroalkylamines of the type $RCF_2NClF$. Characterization of the new compounds $CF_3CF_2NClF$, $CF_3CF_2CF_2NClF$, $(CF_2NClF)_2$, and $CCl_3CF_2NClF$ is reported along with an improved synthesis of $ClCF_2NClF$. The chlorofluorination reaction proceeds mainly via the initial formation of $RNCl_2$, which is then fluorinated in a new type of reaction to give RNClF and ClF.

## Introduction

*N,N*-Dihaloalkylamines are useful synthetic reagents. Many compounds of the type $RNCl_2$[1] and $RNF_2$[2] have been prepared and utilized in a variety of interesting reactions. Mixed *N*-chloro-*N*-fluoroalkylamines, RNClF, are another potentially useful class of reagents which have not been investigated due to lack of suitable methods for their preparation. Only a few examples of *N*-chloro-*N*-fluoroalkylamines are known: $CF_3NClF$,[3,4] $ClCF_2NClF$,[4] $(CF_3)_2CFNClF$,[4] $Cl_2CFNClF$,[4] and $CH_3CF_2NClF$.[5] These compounds are prepared by reaction of the corresponding *N*-fluorimines with ClF,[4] except in the last example which was obtained from $CH_3CN$ and $ClF_5$[5] (eq 1 and 2). In general, the *N*-fluorimines are difficult

$$>C{=}NF + ClF \rightarrow >CFNClF \qquad (1)$$

$$CH_3CN + ClF_5 \rightarrow CH_3CF_2NClF \qquad (2)$$

to obtain and the low-yield reaction with $ClF_5$ has not been extended to other examples. In this paper, a new high-yield synthesis of *N*-chloro-*N*-fluoroalkylamines from the reaction of RCN with a mixture of ClF and $F_2$ is reported[6] (eq 3).

$$RCN + ClF + F_2 \rightarrow RCF_2NClF \qquad (3)$$

This method utilizes two new types of reactions, the addition of fluorine to $RCF{=}NCl$ and the fluorination of $RNCl_2$ to RNClF.

## Experimental Section

**General Methods.** All compounds were handled in Pyrex or stainless-steel vacuum systems equipped with glass–Teflon or stainless-steel valves. Pressures were measured with a precision Heise Bourdon tube gauge in the metal system and a Wallace and Tiernan differential pressure gauge in the glass system. Amounts of volatile compounds were determined by *PVT* measurements with the assumption of ideal gas behavior. Molecular weights were determined by vapor density measurements. Temperatures were measured with a digital read-out copper–constantan thermocouple.

**Table I.** Reaction of RCN with the ClF/$F_2$ Mixture[a]

| RCN | reacn conditions[c] $T$, °C | $t$, h | products (yield, %) |
|---|---|---|---|
| ClCN | 25 | 4 | $ClCF_2NClF$ (94) |
| ClCN | 0 | 10 | $ClCF_2NClF$ (91) |
| ClCN | 25 | 10 | $ClCF_2NClF$ (89) |
| ClCN | 25 | 24 | $ClCF_2NClF$ (66) |
| $CF_3CN$ | 25 | 40 | $CF_3CF_2NClF$ (95) |
| $CF_3CN$ | 25 | 6 | $CF_3CF_2NClF$ (46), $CF_3CN$ (28), $CF_3CF_2NCl_2$ (24) |
| $CF_3CF_2CN$ | 25 | 63 | $CF_3CF_2CF_2NClF$ (89) |
| $(CN)_2$[b] | 25 | 25 | $(CF_2NClF)_2$ (71) |
| $CCl_3CN$ | 25 | 29 | $CCl_3CF_2NClF$ (60) |
| $CH_3CN$[d] | 25 | 1 | $CH_3CF_2NClF$ (12)<br>$CH_3CF_3$ (45) |

[a] A mixture of 3 mmol each of RCN, ClF, and $F_2$. Yields are based on starting RCN. [b] A mixture of 3 mmol of $(CN)_2$ and 6 mmol each of ClF and $F_2$. [c] After the reactor was slowly warmed from −195 to +25 °C for 1 h. [d] When $F_2$ was condensed onto $CH_3CN$ and ClF at −195 °C, a small explosion occurred inside the reactor.

Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer using a 10-cm glass cell fitted with silver chloride windows. NMR spectra were taken at 29 °C on a Varian XL-100-15 spectrometer using trichlorofluoromethane as a solvent and reference. Chemical shifts are reported as $\phi^*$ values.[7]

**Reagents.** The reagents ClCN, $(CN)_2$ (Matheson Co.), $CF_3CN$, and $C_2F_5CN$ (PCR inc.) were from commerical sources and were used as received. $CCl_3CN$ (Columbia Organic Chemical Co.) was distilled before using. Fluorine (Air Products) was passed through a NaF scrubber before use. ClF was obtained by the reaction of equimolar amounts of $F_2$ and $Cl_2$ in a Monel bomb at 230 °C for 18 h. ClF was removed from the reactor at −111 °C to avoid contamination by $Cl_2$ and $ClF_3$. $CF_3CF{=}NCl$[8] and $ClCF_2NCl_2$[9] were prepared by literature methods.

**General Method for the Reaction of RCN with a Mixture of ClF and $F_2$ (Table I).** A dry stainless-steel reactor (75 or 150 mL) was treated with $F_2$ at 25 °C for 5 h. The passivated reactor was then cooled to −195 °C, and 3 mmol of RCN, ClF, and $F_2$ was added in that order. In the case of $(CN)_2$, $(CN)_2$ (3 mmol), ClF (6 mmol),

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and $F_2$ (6 mmol) were added. The reactor was then warmed to 25 °C over 1 h, and the reaction was continued as shown in Table I. The reactor was then cooled to −195 °C, and a small amount of noncondensable gases was pumped out. The reaction products were then separated by GLC using a 10 ft × $^3/_8$ in. column packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P. (In the cases of $CCl_3CN$ and $(CN)_2$, a 1 ft × $^3/_8$ in. column was used.) Characterization of the RNClF compounds follows.

$ClCF_2NClF$: mol wt calcd 153.92, found 155.4; the $^{19}F$ NMR and IR agreed with literature values.[4]

$CF_3CF_2NClF$: bp 35 °C; glass at −195 °C and colorless liquid at −153 °C; mol wt calcd 187.47, found 189.0; vp $\log P_{mm} = 6.3917 - 645.54/T - 90082/T^2$; $\Delta H_{vap} = 5.93$ kcal/mol; $\Delta S_{vap} = 21.5$ eu; IR 1351 (m), 1237 (vs), 1172 (s), 1078 (s), 922 (m), 889 (vw), 799 (vw), 723 (w) cm$^{-1}$; $^{19}F$ NMR $CF_3^{M}CF^{A}F^{B}NClF^{X}$ $\phi^*_M$ 80.9 (dd), $\phi^*_A$ 116.9 (ddq), $\phi^*_B$ 107.1 (dd), $\phi^*_X$ 7.4 (br), $J_{MA} = 1.5$, $J_{MB} = \sim 0$, $J_{MX} = 13$, $J_{AB} = 201$, $J_{AX} = 7$, $J_{BX} = 39$ Hz.

$CF_3CF_2CF_2NClF$: bp 34.4 °C; glass at −195 °C; mol wt calcd 237.48, found 237.5; vp $\log P_{mm} = 5.9206 - 429.39/T - 155460/T^2$; $\Delta H_{vap} = 6.59$ kcal/mol; $\Delta S_{vap} = 21.4$ eu; IR 1339 (m), 1290 (w), 1235 (vs), 1197 (s), 1150 (m), 1137 (m), 1112 (m), 992 (s), 920 (m), 884 (w), 865 (vw), 780 (w), 740 (m), 712 (m), 650 (w) cm$^{-1}$; $^{19}F$ NMR $CF_3^{M}CF_2^{N}CF^{A}F^{B}NClF^{X}$ $\phi^*_M$ 82.2 (ddd), $\phi^*_N$ 125.4 (dd), $\phi^*_A$ 113.9 (dm), $\phi^*_B$ 103.3 (ddq), $\phi^*_X$ 6.5 (br d), $J_{MB} = 10$, $J_{NA} = 3$, $J_{NX} = 16$, $J_{AB} = 204$, $J_{BX} = 43$, $J_{MN} = J_{NB} = \sim 0$, $J_{MA}$ or $J_{AX} = 3.5$ or 7 Hz, $J_{MX}$ not determined.

$(CF_2NClF)_2$ (mixture of diastereoisomers A and B): bp 70 °C; colorless glass at −195 °C; mol wt calcd 236.93, found 238.4; vp data [$T$, °C ($P$, mmHg)] 4.3 (27.3), 14.9 (51.8), 21.2 (70.6), 26.0 (91.7), 32.1 (129.2); IR 1295 (m), 1213 (vs), 1142 (s), 1050 (s), 914 (s) 884 (m), 850 (w), 802 (vw), 764 (sh), 748 (m), 712 (w), 595 (vw) cm$^{-1}$. $^{19}F$ NMR at 29 °C (integration showed ratio of A:B as 4:3) $F^{X}ClNCF^{A}F^{B}CF^{A'}F^{B'}NClF^{X'}$: (A isomer) $\phi^*_X \simeq \phi^*_{X'} = 6.4$ (br), $\phi^*_A = \phi^*_{A'} = 102.5$ (m, 8 lines), $\phi^*_B = \phi^*_{B'} = 111.3$ (m, 14 lines), $J_{AX} = J_{A'X'} = 40$, $J_{AB} = J_{A'B'} = 195$, $J_{BX} = J_{B'X'} = 17$ Hz (other coupling constants not determined); (B isomer) $\phi^*_X \simeq \phi^*_{X'} = 6.4$ (br), $\phi^*_A = \phi^*_{A'} = 102.5$ (m, 8 lines), $\phi^*_B = \phi^*_{B'} = 109.7$ (m, 8 lines), $J_{AX} = J_{A'X'} = 37$, $J_{BX} = J_{B'X'} = 16$, $J_{AB} = J_{A'B'} = 195$, $J_{AX'} = J_{A'X} = 14$, $J_{BX'} = J_{B'X} = 8$ Hz (other coupling constants not determined).

$CCl_3CF_2NClF$: mp −56.0 to −56.5 °C; mol wt calcd 236.84, found 236.0; IR 1204 (vs), 1112 (s), 925 (vw), 938 (s), 871 (w), 846 (vs), 820 (vw), 756 (w), 713 (m), 690 (m) cm$^{-1}$; $^{19}F$ NMR $CCl_3CF^{A}F^{B}NClF^{X}$ $\phi^*_A$ 91.7 (dd), $\phi^*_B$ 110.6 (d), $\phi^*_X$ −3.6 (br d), $J_{AB} = 182$, $J_{AX} = 43$, $J_{BX} = \sim 1$ Hz.

**Reaction of $ClCF_2NCl_2$ with $F_2$.** Fluorine (3 mmol) was condensed onto $ClCF_2NCl_2$ (3 mmol) at −195 °C in the stainless-steel reactor. Then the reactor was warmed to 25 °C over 1 h and stood at 25 °C for 4 h. After a small amount of unreacted $F_2$ and other gases were pumped out at −195 °C, the reaction products were separated through −111 and −195 °C. The product in the −111 °C trap was separated by GLC, giving $ClCF_2NClF$ in 74% yield, with three other unidentified compounds. The molecular weight of the material in the −195 °C trap was 67.0, and the IR spectrum showed the presence of a large amount of ClF with absorptions at 793 and 785 cm$^{-1}$ along with some absorptions from $CF_2Cl_2$ and $SiF_4$.

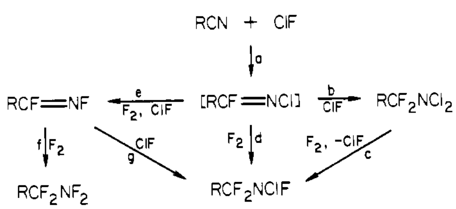
**Reaction of $CF_3CF{=}NCl$ with $F_2$.** Fluorine (1 mmol) was condensed onto $CF_3CF{=}NCl$ (1 mmol) at −195 °C in the stainless-steel reactor. The reactor was warmed to 25 °C over 1 h and kept at 25 °C for 3 h. After a small amount of unreacted $F_2$ was pumped out at −195 °C, the reaction mixture was separated by GLC, giving $CF_3CF_2NClF$ (0.8 mmol) and several unidentified byproducts

## Results and Discussion

The reaction of nitriles with a mixture of $ClF/F_2$ are summarized in Table I. The reactions proceed in excellent yield in all cases except for $CH_3CN$, where explosive side reactions occur. For all halogenated nitriles except ClCN, the overall reaction is quite slow and 1 or more days are required for maximum yields. With ClCN, the optimum reaction time at 25 °C was 4 h on a 3-mmol scale. Longer reaction times decrease the yield, presumably due to some unknown catalytic decomposition of $ClCF_2NClF$. Pure $ClCF_2NClF$ is stable under similar conditions.

The chlorofluorination reactions are not explosive on the scale indicated except for $CH_3CN$. Attempts to scale up the reactions of $CF_3CN$ and $C_2F_5CN$ however resulted in explosions. This is believed to be due to difficulties in controlling the reaction conditions. This was partially confirmed by a 10-mmol scale reaction of $CF_3CN$, where the fluorine was added in five aliquots. The overall yield of $CF_3CF_2NClF$, however, was reduced to 62%. A two-chamber reactor in which the $F_2$ would be added over a short time (but not so fast as to give a liquid phase) to the $CF_3CN/ClF$ mixture, as it warmed slowly from −195 °C, would probably allow these reactions to be run on a considerably larger scale. In the case of ClCN, the reaction has been carried out on a 30-mmol scale without incident with use of a single reactor. The yields on the large scale remained near 90%.

Scheme I



The sequence of reactions leading to formation of RNClF cannot be stated with certainty, but the Scheme I summarizes some of the possible reactions. The reaction of ClF with RCN (a and b) takes place at very low temperatures, probably near the melting point of ClF (−155 °C), and $RCF_2NCl_2$ derivatives are formed in high yields.[8,9] Intermediates $RCF{=}NCl$ have not been isolated in this study, even when a large excess of RCN is employed. An initial reaction of RCN with $F_2$ instead of ClF cannot be of much importance since ClCN can be recovered in 80% yield when allowed to stand with $F_2$ for 4 h at 25 °C. In the latter case, seven products were observed by GLC and it is noteworthy that four of these have retention times identical with those of minor products found in the reaction of ClCN with $F_2/ClF$. Reaction e is not observed to any extent when a known sample of $RCF{=}NCl$ is allowed to react with $F_2$. Reaction f, while a known reaction,[8,10] is also unimportant since no $RCF_2NF_2$ compounds have been found in any of the reactions studied. Reactions c and d have been confirmed independently for several cases and details are given in the Experimental Section for $CF_3CF{=}NCl/F_2$ and $ClCF_2NCl_2/F_2$.[8] From the short-reaction-time run with $CF_3CN$, it can be assumed that reaction path a–b–c is the main sequence by which $RCF_2NClF$ is formed. However, reaction d may also be of some importance. In this regard, it can be noted that yields of RNClF are always lower when reactions a + b and c are carried out in sequence.

The reaction of $NCl_2$ compounds with $F_2$ (c) to form ClF and NClF is apparently quite general, and it has been extended to noncarbon systems.[11] To our knowledge, there have been no previously published reports of this reaction type, although attempts have been made to fluorinate $NCl_2$ groups with other fluorinating reagents.[12] The reaction is unusual in that chlorine is replaced by fluorine with a concomitant increase in the oxidation state of nitrogen by one unit.[13] Further oxidation and substitution of the second chlorine has a much greater activation energy, as no evidence has been found for $NF_2$ derivatives at 25 °C or lower. The uncatalyzed addition of $F_2$ to $>C{=}N-$ systems (d) in a static system has also apparently not been previously recognized as a useful reac-

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(12) DeMarco, R. A.; Shreeve, J. M. *J. Fluorine Chem.* **1971**, *1*, 269.

(13) The positive nature of the chlorine in $CF_3NCl_2$, and therefore the formal assignment of a +1 oxidation state to chlorine in this and related compounds, is clear from chemical evidence, e.g.: Kloter, G.; Seppelt, K. *J. Am. Chem. Soc.* **1979**, *101*, 347.

**Table II**

| $RCF^AF^BNClF$ | $J_{AB}$, Hz | $\Delta_{AB}/J_{AB}$ |
|---|---|---|
| $ClCF_2NClF$[a] | 128 | 2.0 |
| $CF_3CF_2NClF$[b] | 201 | 4.6 |
| $C_2F_5CF_2NClF$[b] | 204 | 4.9 |
| $CCl_3CF_2NClF$[b] | 182 | 9.8 |
| $FClNCF_2CF_2NClF$ (A)[b] | 195 | 5.0 |
| $FClNCF_2CF_2NClF$ (B)[b] | 195 | 3.5 |

[a] Reference 4. [b] This work.

tion.[14] The application of this reaction to a variety of >C═N– derivatives will be reported separately.[8]

All the RNClF derivatives obtained in this work are stable, colorless liquids at 22 °C. None have shown any tendency to explode, although caution is advised in handling these materials. In NMR studies, $CCl_3CF_2NClF$ did not decompose at 100 °C in $CCl_4$, and $(CF_2NClF)_2$ was stable in $CFCl_3$ at 60 °C, the highest temperature used. The stability of $ClCF_2NClF$ was examined in some detail, since previous reports indicated the compound eliminated $Cl_2$ at 25 °C.[4] We found that pure $ClCF_2NClF$ is stable at 25 °C in glass or fluorine-passivated stainless-steel and that the compound is unaffected by ordinary room light. At 100 °C in Pyrex, the compound was recovered quantitatively after 1 day. The previously observed instability must therefore have been due to impurities. This is consistent with long-reaction-time studies done with $ClCN/ClF/F_2$, where the yield decreased markedly after standing 1 day as compared to a 4-h reaction time.

The $^{19}F$ NMR spectra of $RCF_2NClF$ provide additional evidence for the high barriers to inversion observed in fluorinated amines.[4,15] The asymmetric nitrogen atom causes the two methylene fluorines to be diastereotopic, as long as the rate of inversion at nitrogen is slow on the NMR time scale. As was previously observed for $ClCF_2NClF$ and $(CF_3)_2CFNClF$, this gives rise to ABX-type spin systems with a large geminal F–F coupling.[4] As long as there are two fluorine atoms on the $\alpha$-carbon, the inversion barrier will be quite high in perhalogenated systems.[16]

In previous work with $(CF_3)_2CFNClF$, equivalence of the $CF_3$ groups was observed at 60 °C, whereas $ClCF_2NClF$ did not exhibit coalescence up to 100 °C.[4] In this work, $CCl_3CF_2NClF$ was heated to 100 °C in $CCl_4$, where the two methylene fluorines were still separated by 1750 Hz and had moved only 20 Hz toward the center as compared to the 29 °C spectrum. In $(CF_2NClF)_2$ the NMR spectrum shows the presence of two diastereomers which we have labeled A and B. They are not formed in equal amounts, which is reasonable considering that the compound is probably formed by the stepwise fluorination of the intermediate $(CF_2NCl_2)_2$. The NMR for the two diastereomers can be considered that of two AA′BB′XX′ spin systems. Not all the coupling constants could be evaluated, and the values given in the Experimental Section are only approximate except for $J_{AB}$ and $J_{A'B'}$, which could be easily determined from the experimental spectra. Heating this sample to 60 °C caused the $CF_2$ multiplets of isomer A to move 22 Hz to the center while the change in isomer B was only 5 Hz. For comparison, the $\Delta_{AB}/J_{AB}$ values for the known perhaloamines of the type $RCF^AF^BNClF$ are given in Table II.

## Summary

In summary a wide variety of *N*-chloro-*N*-fluoroperhaloalkylamines can now be prepared in excellent yield. The chlorofluorination reaction can probably be used with nearly any perhalogenated cyano derivative. These new amines are expected to have an interesting reaction chemistry via the reactivity of the N–Cl bond, and they are the precursors to the high-yield synthesis of *N*-fluorimines and *N*-fluoramines.[6,8]

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**Registry No.** $ClCF_2NClF$, 33757-11-8; $CF_3CF_2NClF$, 13880-72-3; $CF_3CN$, 353-85-5; $CF_3CF_2NCl_2$, 677-66-7; $CF_3CF_2CF_2NClF$, 72306-69-5; $(CF_2NClF)_2$ (isomer 1), 75347-90-9; $CCl_3CF_2NClF$, 75347-91-0; $CH_3CF_2NClF$, 16276-45-2; $CH_3CF_3$, 420-46-2; ClCN, 506-77-4; $CF_3CF{=}NCl$, 650-50-0; $CF_3CF_2CN$, 422-04-8; $(CN)_2$, 460-19-5; $CCl_3CN$, 545-06-2; $CH_3CN$, 75-05-8; ClF, 7790-89-8; $F_2$, 7782-41-4; $ClCF_2NCl_2$, 28245-34-3.

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(14) There are many reports on the reaction of $F_2$ with unsaturated carbon–nitrogen compounds[2] using flow systems and/or metal fluoride catalysts.

(15) Griffith, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4089. Johnson, F. A.; Haney, L.; Stevens, T. E. *J. Org. Chem.* **1967**, *32*, 466.

(16) In $CH_3CF_2NClF$, the $^{19}F$ NMR of the $CF_2$ group is a basic quartet with some additional splitting. The $CF_2$ group does not exhibit the expected $ABXM_3$ second-order pattern, implying that the inversion rate at nitrogen is fast at ~30 °C or that the chemical shifts are accidentally degenerate.

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# Circumnavigation of Uranylhexafluoroacetylacetonate by Lewis Bases

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The chelated uranylhexafluoroacetylacetonate ion forms adducts with Lewis bases which are fluxional when studied by $^{19}F$ NMR. The compounds have a pentagonal-bipyramidal geometry in which the base occupies one site in the equatorial ring. The kinetic parameters suggest that the equilibrating process is one in which the base migrates to a complementary site on the other side of the uranyl ion via intermediate capped octahedral structures.

The tetrahydrofuran adduct of uranylhexafluoroacetylacetonate, **1**, has recently been described.[1] An X-ray crystal structure determination revealed a linear $UO_2^{2+}$ ion surrounded equatorially by a pentagonal array of the five oxygen atoms contributed by the pair of bidentate anions and the tetrahydrofuran molecule. In this configuration there are $CF_3$ and carbonyl groups both near and remote from the THF molecule, and NMR studies might be expected to display a magnetic inequality between them. At ambient temperatures in nonpolar solvents, however, both $^{19}F$ and $^{13}C$ NMR studies indicate single sharp resonances for the $CF_3$ and carbonyl groups.

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