

**AN IMPROVED SYNTHESIS OF DICHLOROFLUORAMINE,  $\text{FNCl}_2$** \*

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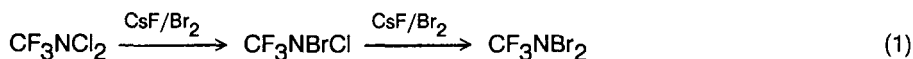
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**SUMMARY**

Low-temperature fluorination of *N,N*-dichloro-1-fluoroformamide,  $\text{FC(O)NCl}_2$ , has provided a more convenient, high-yield (75%) synthesis of dichlorofluoramine,  $\text{FNCl}_2$ , than was previously available. In an attempt to further expand the novel metal fluoride promoted conversion of N-Cl bonds to N-Br bonds, both  $\text{FC(O)NCl}_2$  and  $\text{FNCl}_2$  were reacted with bromine in the presence of various alkali metal fluorides. No evidence was found for the formation of either  $\text{FC(O)NBrCl}$  and  $\text{FC(O)NBr}_2$  or  $\text{FNBrCl}$  and  $\text{FNBr}_2$  in these reactions. In fact,  $\text{FC(O)NCl}_2$  was found to decompose to  $\text{C(O)F}_2$ ,  $\text{N}_2$ , and  $\text{Cl}_2$  in the presence of alkali metal fluorides.

**INTRODUCTION**

In 1984 Zheng *et al.* reported a novel fluoride promoted conversion of N-Cl bonds to N-Br bonds as shown in eqn. (1) [1]. It then became of interest



to see whether or not this methodology could be extended to the preparation of unknown *N*-halo amines such as  $\text{FNBrCl}$  and  $\text{FNBr}_2$ . However, before this investigation could be carried out, it was deemed necessary to find a more convenient and safer method of preparing laboratory quantities of dichlorofluoramine,  $\text{FNCl}_2$ . The results of this investigation are reported herein.

## EXPERIMENTAL

The compound  $\text{FC(O)NCl}_2$  was prepared by literature methods [2]. Cesium fluoride (99.9%) was activated by fusing in a Pt dish, followed by grinding in jar mill to a very fine powder under anhydrous conditions, while NaF was taken from laboratory stock and dried *in vacuo*. Bromine was dried over  $\text{P}_2\text{O}_5$  and distilled prior to use.

**Caution!** Many *N*-halo compounds are known to be powerful explosives; therefore, suitable safety precautions should be kept in mind. We advise that the preparations and reactions of these materials be done on a small scale.

Infrared spectra were obtained on a Perkin-Elmer 1430 Data System; a 10-cm glass cell fitted with KCl windows was employed. Mass spectra were taken on a HP 5895A GC-MS system.  $^{19}\text{F}$  NMR spectra were recorded on a JEOL FX-90 Q spectrometer at 84.25 MHz and referenced to internal  $\text{CCl}_3\text{F}$ .

### Synthesis of dichlorofluoramine, $\text{FNCl}_2$

The dichloroamide  $\text{FC(O)NCl}_2$  (3.0 mmol) was condensed into the bottom of a 150 mL stainless steel cylinder chilled to liquid-nitrogen temperature. The level of the liquid nitrogen was then raised and a slight excess of elemental fluorine (3.5 mmol) was slowly added. The reaction vessel was placed in a Dewar of evaporating liquid nitrogen and allowed to warm slowly to room temperature overnight. The vessel was then recharged to  $-196^\circ\text{C}$  and attached to the vacuum line where any noncondensable materials were removed through a scrubber filled with soda lime. The condensable materials were then transferred to the vacuum system and passed through a series of traps at  $-80$ ,  $-115$  to  $-120$ , and  $-196^\circ\text{C}$ . The trap at  $-80^\circ\text{C}$  stopped 0.1 mmol of unreacted  $\text{FC(O)NCl}_2$ , while the trap maintained at between  $-115$  and  $-120^\circ\text{C}$  held the desired product  $\text{FNCl}_2$  (2.25 mmol) in 75% yield. The identity and purity of the  $\text{FNCl}_2$  was ascertained primarily through infrared spectroscopy [3]. The  $-196^\circ\text{C}$  trap contained (3.5 mmol) primarily  $\text{COF}_2$ .

### Reactions of $\text{FC(O)NCl}_2$ and $\text{FNCl}_2$ with $\text{Br}_2$ and/or $\text{MF}$ , where $\text{M} = \text{Na, Cs}$

In a typical reaction (see Table 1), NaF (0.1 g; 2.38 mmol) was loaded into a 250-mL glass vessel in a drybox under nitrogen atmosphere. The vessel was then evacuated, and  $\text{FC(O)NCl}_2$  (0.5 mmol) was condensed in at  $-196^\circ\text{C}$ . The reaction

TABLE 1

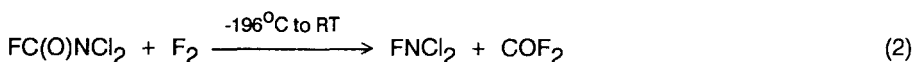
Reactions of  $\text{FC(O)NCl}_2$  and  $\text{FNCI}_2$  with  $\text{Br}_2$  and/or MF, where M = Na, Cs

Reactants (mmol)		Conditions ( $^{\circ}\text{C}/\text{h}$ )	Volatile Products (mmol)
$\text{FC(O)NCl}_2$ (0.5)	$\text{Br}_2$ (2.0)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/12 h	No Reaction
$\text{FC(O)NCl}_2$ (4.8)	CsF (10.0)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/12 h	IR - $\text{COF}_2$ noncondensibles - $\text{N}_2$
$\text{FC(O)NCl}_2$ (0.5)	NaF (2.38)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/12 h	$\text{COF}_2$ (0.5), $\text{Cl}_2$ (0.25) noncondensibles - $\text{N}_2$
$\text{FC(O)NCl}_2$ (5.0)	NaF (15.0)/ $\text{Br}_2$ (10.0)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/ 12 h	IR - $\text{COF}_2$ noncondensibles - $\text{N}_2$ unreacted $\text{Br}_2$
$\text{FC(O)NCl}_2$ (4.8)	CsF (10.0)/ $\text{Br}_2$ (10.0)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/12 h	IR - $\text{COF}_2$ noncondensibles - $\text{N}_2$ unreacted $\text{Br}_2$
$\text{FNCI}_2$ (2.0)	CsF (5.0)/ $\text{Br}_2$ (5.0)	$-196^{\circ}\text{C}$ to RT/2-3 h RT/12 h	IR - $\text{FNO}_2$ (trace) [8] IR - $t\text{-N}_2\text{F}_2$ (trace) [9] noncondensibles- $\text{N}_2$ unreacted $\text{Br}_2$ & $\text{BrCl}$
$\text{FNCI}_2$ (2.25)	CsF (5.0)/ $\text{Br}_2$ (5.0)	$-196^{\circ}\text{C}$ to $-50^{\circ}\text{C}$ /2-3 h $-40^{\circ}\text{C}$ /3 h & $-30^{\circ}\text{C}$ /12 h $0^{\circ}\text{C}$ /12 h $10^{\circ}\text{C}$ /12 h	unreacted $\text{FNCI}_2$ (1.16) noncondensibles (0.55) unreacted $\text{Br}_2$ & $\text{BrCl}$

mixture was allowed to warm slowly to room temperature and react overnight. The volatile products were then moved to the vacuum line for trap-to-trap distillation. Lots of noncondensibles, presumably nitrogen, were removed during this process. The remaining condensibles, which were yellow in color, were then transferred to a trap containing mercury in order to test for the presence of chlorine. Approximately, one-third or 0.25 mmol of the condensibles were scrubbed by the mercury, and the remaining condensibles (~0.5 mmol) were shown by infrared spectroscopy to be predominantly  $\text{COF}_2$ .

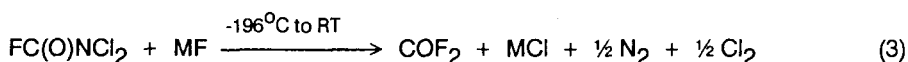
## RESULTS AND DISCUSSION

The need for an improved synthesis of  $\text{FNCI}_2$  was recently made obvious in a report to this Journal by Gibert and co-workers [4]. In this paper, the authors overview the previous routes to  $\text{FNCI}_2$  and describe their modifications to a route originally reported by Pankratov and Sokolov [5], namely the fluorination of  $\text{NH}_4\text{Cl}$ . Although this method avoids the dangers associated with preparing  $\text{FNCI}_2$  from  $\text{NaN}_3$  and  $\text{ClF}$  [6] (explosive intermediate  $\text{ClN}_3$  [7]), it still suffers from both relatively low yields and difficulties in the separation of  $\text{FNCI}_2$  from other side products such as  $\text{ClNF}_2$  and  $\text{Cl}_2$  [4]. In our investigation, we found that laboratory quantities of  $\text{ClNF}_2$  could be produced in 75% yield from the low-temperature fluorination of  $\text{FC(O)NCl}_2$  (eq 2). In addition, the product is easily separated from any unreacted starting



materials as well as the  $\text{COF}_2$  and any other by-products formed.

The reactivity of  $\text{FC(O)NCl}_2$  in the presence of bromine and alkali metal fluorides both separately and together was then studied in an attempt to prepare  $\text{FC(O)NBrCl}$  and/or  $\text{FC(O)NBr}_2$ . The formation of either of these new haloamines was precluded by the more ready decomposition of  $\text{FC(O)NCl}_2$  in the presence of fluoride ion as shown in equation 3. This observation is not surprising in view of the



fact that the decomposition of  $\text{FC(O)NSF}_2$  to  $\text{COF}_2$  and  $\text{NSF}$  is known to take place at temperatures as low as  $0^\circ\text{C}$  in the presence of cesium fluoride [10]. The reaction

of  $\text{FNOCl}_2$  with  $\text{Br}_2$  and  $\text{CsF}$  failed to produce any evidence for either  $\text{FNOBrCl}$  or  $\text{FNOBr}_2$  under conditions tried (see Table 1). Again, large amounts of noncondensable gas were formed during each reaction.

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