

AN IMPROVED SYNTHESIS OF DICHLOROFLUORAMINE, FNCl₂*

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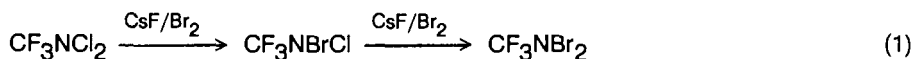
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SC 30634-1905 (U.S.A.)**SUMMARY**

Low-temperature fluorination of *N,N*-dichloro-1-fluoroformamide, FC(O)NCl₂, has provided a more convenient, high-yield (75%) synthesis of dichlorofluoramine, FNCl₂, 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 FC(O)NCl₂ and FNCl₂ were reacted with bromine in the presence of various alkali metal fluorides. No evidence was found for the formation of either FC(O)NBrCl and FC(O)NBr₂ or FNBrCl and FNBr₂ in these reactions. In fact, FC(O)NCl₂ was found to decompose to C(O)F₂, N₂, and Cl₂ 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 FNBrCl and FNBr₂. 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, FNCl₂. The results of this investigation are reported herein.

EXPERIMENTAL

The compound 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 P_2O_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}F NMR spectra were recorded on a JEOL FX-90 Q spectrometer at 84.25 MHz and referenced to internal CCl_3F .

Synthesis of dichlorofluoramine, FNCl_2

The dichloroamide 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°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°C . The trap at -80°C stopped 0.1 mmol of unreacted FC(O)NCl_2 , while the trap maintained at between -115 and -120°C held the desired product FNCl_2 (2.25 mmol) in 75% yield. The identity and purity of the FNCl_2 was ascertained primarily through infrared spectroscopy [3]. The -196°C trap contained (3.5 mmol) primarily COF_2 .

Reactions of FC(O)NCl_2 and FNCl_2 with Br_2 and/or MF, where M = 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 FC(O)NCl_2 (0.5 mmol) was condensed in at -196°C . The reaction

TABLE 1

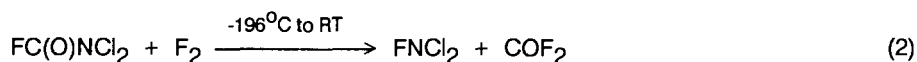
Reactions of FC(O)NCl_2 and FNCl_2 with Br_2 and/or MF, where M = Na, Cs

Reactants (mmol)		Conditions ($^{\circ}\text{C}/\text{h}$)	Volatile Products (mmol)
FC(O)NCl_2 (0.5)	Br_2 (2.0)	-196°C to RT/2-3 h RT/12 h	No Reaction
FC(O)NCl_2 (4.8)	CsF (10.0)	-196°C to RT/2-3 h RT/12 h	IR - COF_2 noncondensibles - N_2
FC(O)NCl_2 (0.5)	NaF (2.38)	-196°C to RT/2-3 h RT/12 h	COF_2 (0.5), Cl_2 (0.25) noncondensibles - N_2
FC(O)NCl_2 (5.0)	NaF (15.0)/ Br_2 (10.0)	-196°C to RT/2-3 h RT/ 12 h	IR - COF_2 noncondensibles - N_2 unreacted Br_2
FC(O)NCl_2 (4.8)	CsF (10.0)/ Br_2 (10.0)	-196°C to RT/2-3 h RT/12 h	IR - COF_2 noncondensibles - N_2 unreacted Br_2
FNCl_2 (2.0)	CsF (5.0)/ Br_2 (5.0)	-196°C to RT/2-3 h RT/12 h	IR - FNO_2 (trace) [8] IR - $t\text{-N}_2\text{F}_2$ (trace) [9] noncondensibles- N_2 unreacted Br_2 & BrCl
FNCl_2 (2.25)	CsF (5.0)/ Br_2 (5.0)	-196°C to -50°C /2-3 h -40°C /3 h & -30°C /12 h 0°C /12 h 10°C /12 h	unreacted FNCl_2 (1.16) noncondensibles (0.55) unreacted Br_2 & 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 COF_2 .

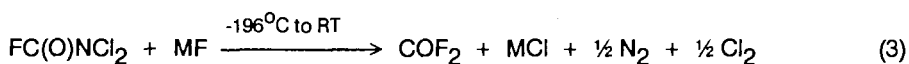
RESULTS AND DISCUSSION

The need for an improved synthesis of FNCl_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 FNCl_2 and describe their modifications to a route originally reported by Pankratov and Sokolov [5], namely the fluorination of NH_4Cl . Although this method avoids the dangers associated with preparing FNCl_2 from NaN_3 and ClF [6] (explosive intermediate ClN_3 [7]), it still suffers from both relatively low yields and difficulties in the separation of FNCl_2 from other side products such as ClNF_2 and Cl_2 [4]. In our investigation, we found that laboratory quantities of ClNF_2 could be produced in 75% yield from the low-temperature fluorination of FC(O)NCl_2 (eq 2). In addition, the product is easily separated from any unreacted starting



materials as well as the COF_2 and any other by-products formed.

The reactivity of 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 FC(O)NBrCl and/or FC(O)NBr_2 . The formation of either of these new haloamines was precluded by the more ready decomposition of 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 FC(O)NSF_2 to COF_2 and NSF is known to take place at temperatures as low as 0°C in the presence of cesium fluoride [10]. The reaction

of FNCl_2 with Br_2 and CsF failed to produce any evidence for either FNBrCl or FNBr_2 under conditions tried (see Table 1). Again, large amounts of noncondensable gas were formed during each reaction.

ACKNOWLEDGEMENT

We thank Dr. K. O. Christe for a preprint of his article prior to publication. D.D.D. gratefully acknowledged the financial support of the U.S. Army Research Office and the National Science Foundation.

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