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AN IMPROVED SYNTHESIS OF DICHLOROFLUORAMINE, $FNCl_2$*

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SUMMARY

Low-temperature fluorination of *N,N*-dichloro-1-fluoroformamide, $FC(O)NCl_2$, has provided a more convenient, high-yield (75%) synthesis of dichlorofluoramine, $FNCl_2$, 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 $FC(O)NCl_2$ and $FNCl_2$ 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 $FC(O)NBr_2$ or $FNBrCl$ and $FNBr_2$ in these reactions. In fact, $FC(O)NCl_2$ was found to decompose to $C(O)F_2$, N_2, and Cl_2 in the presence of alkal 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

$$CF_3NCl_2 \xrightarrow{CsF/Br_2} CF_3NBrCl \xrightarrow{CsF/Br_2} CF_3NBr_2 \qquad (1)$$

to see whether or not this methodology could be extended to the preparation of unknown *N*-halo amines such as $FNBrCl$ and $FNBr_2$. 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, $FNCl_2$. The results of this investigation are reported herein.

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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 rechilled to -196°C and attached to the vacuum line where any noncondensible materials were removed through a scrubber filled with soda lime. The condensible 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 (°C/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-N_2F_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.

$$FC(O)NCl_2 + F_2 \xrightarrow{-196^{o}C \text{ to RT}} FNCl_2 + COF_2 \qquad (2)$$

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 $0^{o}C$ in the presence of cesium fluoride [10]. The reaction

$$FC(O)NCl_2 + MF \xrightarrow{-196^{o}C \text{ to RT}} COF_2 + MCl + \tfrac{1}{2} N_2 + \tfrac{1}{2} Cl_2 \qquad (3)$$

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 noncondensible gas were formed during each reaction.

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