much slower when Ba^{2+} is a reactant than it is when Pb^{2+} or Hg^{2+} react. The difference is in line with the greater capacity Hg^{2+} or Pb^{2+} have compared to Ba^{2+} in polarizing associated ligands. Some related observations are these: Ag^+ reacts rapidly with $(NH_3)_5CoCO_3^+$; the reactions of Ni^{2+}, Cu^{2+}, or Co^{2+} with the carbonato complex are even slower than that of Ba^{2+}; Pb^{2+} reacts with $en_2CoCO_3^+$ to form $PbCO_3$, but the reaction is slower than that with the pentaammine.

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CONTRIBUTION FROM HYNES CHEMICAL RESEARCH
CORPORATION, DURHAM, NORTH CAROLINA

The Addition of Chlorine Monofluoride to Fluorinated Nitriles

BY JOHN B. HYNES AND THOMAS E. AUSTIN

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Fluorinated analogs of the alkyl dichloramines have received only cursory attention in the recent literature and the two known examples, CF_3NCl_2 and $C_2F_5NCl_2$, were prepared by rather difficult routes. For example, the high-pressure reaction of silver(I) fluoride and chlorine with ClCN or CF_3CN produced CF_3NCl_2 and $C_2F_5NCl_2$ in low yields.[1] The reaction of ClCN with silver(II) fluoride and excess chlorine resulted in an improved yield of CF_3NCl_2 (30%).[2]

We wish to report a general synthesis of fluorinated aliphatic dichloramines which involves the low-temperature addition of chlorine monofluoride to fluorinated nitriles. Using this technique, $C_2F_5NCl_2$, $C_3F_7NCl_2$, $CClF_2CF_2NCl_2$, and $NCl_2CF_2CF_2CF_2NCl_2$ have been prepared in 65 to 75% yield with only a very small percentage of by-product formation accompanying the reactions. The generalized equation for this transformation is

$$RCN + 2ClF \longrightarrow RCF_2NCl_2$$

Although these compounds rapidly oxidize aqueous potassium iodide solutions, they were found not to be appreciably impact sensitive.

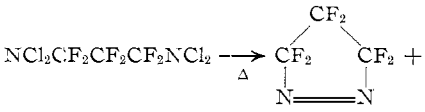
Two observations help to elucidate the mechanism of this reaction. First, when a 1:1 molar ratio of the reactants was employed, no RCF=NCl compounds were detected. This result was not unexpected, however, since the imine should be considerably more susceptible to addition than the corresponding nitrile, as has been observed in a number of fluorination studies. Secondly, evidence for the imine intermediate is furnished by the fact that no azo compounds of the type $RCF_2N{=}NCF_2R$ were formed in any of the experiments. This fact seems to preclude the path whereby chlorine monofluoride fluorinates the nitrile carbon to produce a nitrene intermediate, $RCF_2\ddot{N}$, and chlorine. This latter process always occurs to an appreciable extent when fluorinated nitriles are allowed to react with silver(II) fluoride or with elemental fluorine.[2-5]

In an attempt to compare the reactivity of chlorine monofluoride with that of fluorine, an analogous experiment was performed using fluorine and CF_3CN. Almost complete fluorinolysis of the C–N bond occurred, with C_2F_6 and NF_3 being the major components of a very complex reaction product. Thus, it is apparent that chlorine monofluoride is a considerably less energetic reagent than fluorine when employed at low temperatures in a closed system.

The thermal decomposition of the fluorinated dichloramines proceeded cleanly in the neighborhood of 200° producing chlorine and a symmetrical azo compound in high yield. For example, $CClF_2CF_2NCl_2$ decomposed as follows yielding the known azo compound, $CClF_2CF_2N{=}NCF_2CClF_2$.[3]

$$2CClF_2CF_2NCl_2 \xrightarrow[\Delta]{} CClF_2CF_2N{=}NCF_2CClF_2 + 2Cl_2$$

Under similar conditions the bis(dichloramine) produced the cyclic azo compound, hexafluoro-1-pyrazoline, which was recently prepared in low yield by the action of silver(II) fluoride on $CF_2(CN)_2$.[3] The related four-membered heterocyclic compound, $\underline{CF_2N{=}NCF_2}$, was prepared by the action of silver(II) fluoride on cyanogen.[6]



In addition to providing further structural corroboration for the new dichloramines, this pyrolytic reaction provides a convenient route to otherwise difficultly accessible azo compounds and a potential route to new unsymmetrical and cyclic systems. Further work in these areas is presently in progress.

Experimental Section

Apparatus and Materials.—The addition reactions were conducted in a 150-cc Monel cylinder which was equipped with an M440 Hoke valve and was silver soldered directly to an all-metal vacuum system. Infrared spectra were determined using a Beckman IR-8 spectrophotometer while the ultraviolet absorption spectra were measured with a Beckman DB spectrophotometer. The F^{19} nmr spectra were measured with a Varian high-resolution spectrometer, Model V-4300-2, employing a probe frequency of 56.4 Mc. The chemical shifts are reported in ppm relative to CCl_3F which was used as an internal standard and solvent. Chromatographic separations were made using a Micro-Tek 1500 gas chromatograph. Unless stated otherwise, all analytical separations were made at ambient temperature with a 6 ft ×

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0.25 in. copper column packed with 25% Kel-F No. 10 oil on 60–80 mesh Chromosorb P and a helium flow rate of 60 cc/min. Preparative separations were also performed at ambient temperatures with an 8 ft × 0.5 in. column containing 20% Kel-F No. 10 oil on 60–80 mesh Chromosorb P and a carrier gas flow of 200 cc/min. The molecular weights of volatile compounds were determined by gas density.

The CF_3CN and C_2F_5CN were purchased from Columbia Organic Chemicals Co. while the preparations of $CClF_2CN$[7] and $CF_2(CN)_2$[8] have been described in recent papers. The ClF was purchased from the Ozark-Mahoning Co.

The Reaction of ClF with CF_3CN.—Into the 150-cc cylinder were condensed successively 10 mmoles of CF_3CN and 20 mmoles of ClF. The vessel was then warmed from −196 to −78° and maintained at this temperature for approximately 10 hr after which it was allowed to warm gradually to 0°. The contents of the reactor were degassed at −78° and there remained 0.75 ml of light yellow liquid which was shown chromatographically to be better than 95% $C_2F_5NCl_2$ (estimated yield 75%). A sample purified by preparative chromatography, boiled at 44° (760 mm) (the literature reports 44°[1]), had a molecular weight of 206 (calcd 204), and an ultraviolet absorption maximum at 294 mμ (vapor phase). Its major gas phase infrared bands were located at 1348 (m), 1241 (vs), 1217 (s), 1158 (s), 1075 (vs), 968 (w), 842 (w), 780 (w), 719 (m), and 663 (w) cm^{-1}. The F^{19} nmr spectrum exhibited two peaks, one at +78.4 ppm (CF_3) and the other at +101.2 ppm (CF_2), the relative areas of which were in the ratio of 3.00:2.15.

An analogous experiment was performed using equal molar quantities of the reactants in the hope of preparing the known 1:1 addition compound, $CF_3CF{=}NCl$.[1] However, the resulting mixture was found to contain only $C_2F_5NCl_2$ and CF_3CN and traces of unreacted ClF.

The Reaction of ClF with C_2F_5CN.—Using the same procedure employed with CF_3CN, 10 mmoles of nitrile and 20 mmoles of ClF were allowed to react to produce, after degassing at −78°, 0.8 ml of light yellow liquid. Analysis by infrared and chromatography showed that, in addition to $C_3F_7NCl_2$, a small amount (5–10%) of an unidentified compound exhibiting an absorption band at 1613 cm^{-1} was also produced. Purification by preparative chromatography eliminated this impurity and yielded $C_3F_7NCl_2$ which boiled at 66.2° (757 mm), had a molecular weight of 246, 257 (calcd 254), and a vapor phase ultraviolet absorption maximum at 294 mμ, the estimated yield being 65%. Its nmr spectrum exhibited peaks at +82.4 ppm (CF_3), +97.7 ppm (α-CF_2), and +121.8 ppm (β-CF_2), the areas of which were in the ratio of 3.00:1.96:1.92. The gas phase infrared spectrum showed the following major peaks: 1348 (m), 1289 (w), 1250–1240 (vs), 1205 (s), 1143 (s), 1115 (s), 1035 (s), 990 (s), 968 (s), 833 (w), 767 (w), 735 (m), 709 (m), and 632 (w) cm^{-1}.

The Reaction of ClF with $CClF_2CN$.—This reaction was conducted in a like manner using 10 mmoles of $CClF_2CN$ and 20 mmoles of ClF. However, the resulting reaction mixture was allowed to remain at ambient temperature for 2 days. After degassing several times at −78°, 0.85 ml of liquid product remained in the reactor. The $CClF_2CF_2NCl_2$ was purified from several trace impurities by preparative gas chromatography, the estimated yield being 70%. The purified compound boiled at 85° (760 mm), had a molecular weight of 215 (calcd 220.5), and exhibited a vapor phase ultraviolet absorption maximum at 296 mμ. The F^{19} nmr spectrum showed peaks at +64.2 ppm ($CClF_2$) and +99.1 ppm (CF_2), the relative areas of which were in the ratio of 2:2.04. Its gas phase infrared spectrum showed major peaks at 1276 (m), 1198 (s), 1184 (s, sh), 1150 (s), 1102 (s), 988 (s), 943 (m), 830 (w), 752 (w), 720 (s), 672 (w), and 642 (w) cm^{-1}.

The Reaction of ClF with $CF_2(CN)_2$.—A 4-mmole sample of $CF_2(CN)_2$ and 16 mmoles of ClF were condensed successively into the reactor. After being held at −78° for 10 hr the reactor was allowed to warm slowly to room temperature and left at ambient temperature for 24 hr. After degassing at −78° to remove traces of $CF_2(CN)_2$, the product was transferred with pumping and heating to a glass system yielding 0.45 ml of high-boiling yellow liquid. Analytical chromatography on a 6 ft × 0.25 in. o.d. column packed with 20% Kel-F grease on 60–80 mesh Chromosorb P maintained at 70° showed only one significant component. Vacuum distillation produced a single fraction boiling at 77–78° (28 mm) with an ultraviolet absorption maximum at 298 mμ (CCl_4) and a molecular weight (cryoscopic in benzene) of 296 (calcd 320). Its infrared spectrum (liquid film) showed bands at 1290 (w), 1257 (m), 1191 (vs), 1148 (s), 1113 (m), 1088 (s), 968 (m), 948 (s), 935 (m), 834 (m), 818 (m), 749 (m), 712 (m), 677 (m), and 633 (m) cm$^-$. The F^{19} nmr spectrum exhibited peaks at +97.0 ppm (α-CF_2) and +112.7 ppm (β-CF_2), the relative areas of which were in the ratio of 4.10:2.

Thermal Decomposition of N,N-Dichloramines.—The pyrolytic reactions were conducted in a 150-cc Pyrex vessel equipped with a Fischer and Porter high-pressure needle valve. In each case approximately 0.25 ml of liquid compound was used and the resulting gaseous mixtures were analyzed chromatographically, the products being identified by their known infrared spectra. In all cases chlorine and an azo compound were the principal products, although traces of by-products (<5%) were detected in several cases.

TABLE I

CONDITIONS AND RESULTS OF THE PYROLYSIS OF FLUORINATED N,N-DICHLORAMINES

Reactant	Temp, °C	Duration hr	% reacted	Azo products
$CClF_2CF_2NCl_2$	110	20	0	. . .
$CClF_2CF_2NCl_2$	160 ± 10	63	45	$CClF_2CF_2N{=}NCF_2CClF_2$[3]
$CClF_2CF_2NCl_2$	200 ± 10	24	>95	$CClF_2CF_2N{=}NCF_2CClF_2$[3]
$C_3F_7NCl_2$	205 ± 5	20	85	$C_3F_7N{=}NC_3F_7$[1]
$C_2F_5NCl_2$	200 ± 10	30	90	$C_2F_5N{=}NC_2F_5$[4]
$NCl_2CF_2CF_2CF_2NCl_2$	200–215	63	>95	$\underline{CF_2CF_2CF_2N{=}N}$[3]

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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA

A Study of Bis(hexafluoroacetylacetonato)copper(II)[1]

BY J. A. BERTRAND AND ROY I. KAPLAN

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Although bis(hexafluoroacetylacetonato)copper(II) has been the subject of several studies,[2-4] there appears to be some confusion about the characterization

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