pared the data and powder patterns (private correspondence) and agrees with us that the materials obtained by the two methods must be the same even though the reported powder patterns are not exactly the same.

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The Fluorination of Cyanogen Chloride[1]

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This report describes the results of a study of the direct and indirect fluorination, employing elemental fluorine or AgF_2, respectively, of the relatively reactive chlorinated nitrile, cyanogen chloride, which is also the most simply chlorinated nitrile. It was shown earlier that the direct fluorination of a number of halonitriles[2] yielded both saturated and unsaturated products containing chlorine and also that direct fluorination of the closely related HCN[3] produced not only CF_3NF_3 in good yield, but also $CF_3N{=}NCF_3$, $(CF_3)_2NF$, and $(CF_3)_3N$. The indirect fluorination of ClCN has been the subject of a number of earlier investigations. In each case the nature of the products formed was markedly dependent upon the experimental conditions and the fluorinating agent employed. For example, when ClCN was passed over AgF_2 at near ambient temperature, $CF_3N{=}NCF_3$ was produced in high yield together with some CF_3NO.[4] However, the analogous reaction with HgF_2 at 290–300° produced $CF_3N{=}CF_2$ and $[(CF_3)_2N]_2Hg$, while CuF_2 at 450° gave cyanuric fluoride,[5] but in none of these cases were any organic compounds isolated which contained chlorine. The autoclave reaction of ClCN with AgF in the presence of chlorine yielded a number of products including CF_3Cl and $CF_3N{=}NCF_3$, together with a small amount of a compound partially characterized as CF_3NCl_2.[6]

It was felt that a further study of both the direct and indirect fluorination of cyanogen chloride might lead to the formation of new and interesting fluorinated derivatives of this compound which also contain chlorine. Accordingly, the direct fluorination of cyanogen chloride was undertaken under mild operating conditions in the jet reactor; *cf.* the Experimental Section. The crude product was separated into portions by rectification, and these were then resolved into their components by gas chromatography. The new compounds produced were the saturated adduct, $CClF_2NF_2$, isolated only in small amount, its isomer, CF_3NClF, bp −32.8°, and the azo compound, $CClF_2N{=}NCF_3$, bp 5.8°.[7] They were accompanied by the expected cleavage products, CF_4, $CClF_3$, CCl_2F_2 and $CF_3N{=}NCF_3$, as well as some free chlorine. It is worthy of note that this appears to be the first time that an organic compound of the general formula RNClF has been reported. Apparently, some chlorine is always displaced from the ClCN giving rise to the nitrene, $CF_3N{:}$. This in turn could add ClF, or its component elements, to produce the unexpected compound CF_3NClF.

A comparison of the more significant ions from the mass cracking patterns of the isomers $CClF_2NF_2$ and CF_3NClF appears in Table I. The chlorine isotope ratios were consistent with the ion assignments but the Cl^{37+} ions have been omitted for the sake of brevity.

TABLE I

COMPARATIVE MASS CRACKING PATTERNS OF THE ISOMERS $CClF_2NF_2$ AND CF_3NClF

		Relative Intensities	
m/e	Probable ion	$CClF_2NF_2$	CF_3NClF
31	CF^+	15.0	4.2
33	FN^+	2.8	0.3
35	Cl^+	9.9	3.0
47	CCl^+	1.0	...
49	ClN^+	2.0	35.4
50	CF_2^+	13.6	3.5
52	F_2N^+	1.1	...
64	CF_2N^+	4.9	2.0
66	$CClF^+$	1.6	...
69	CF_3^+	100.0	100.0
83	CF_3N^+	9.1	1.0
85	$CClF_2^+$	44.3	...
99	$CClF_2N^+$	2.6	2.3
102	CF_4N^+	37.7	...
137	$CClF_4N^+$	...	1.6

As seen, these structures are clearly differentiated by the presence or absence of particular ions such as CCl^+, F_2N^+, $CClF^+$, $CClF_2^+$, and CF_4N^+. The formation of the CF_4N^+ ion from $CClF_2NF_2$ in relatively high intensity shows that the loss of chlorine constitutes a primary ionization step for this molecule. The chlorine in CF_3NClF is more difficultly removed as evidenced by the large intensity of the ClN^+ ion and a parent ion which was not exhibited by its isomer. As is true for almost all highly fluorinated organic compounds, the CF_3^+ ion is the most abundant fragment for each compound.

The fluorination of nitriles with AgF_2 in a closed system has been shown to involve nitrene intermediates which dimerize to form azo compounds as prin-

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(1) This material was presented to the Fluorine Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964. This work was supported by the Advanced Research Projects Agency through the Army Research Office (Durham), to whom grateful acknowledgment is hereby made.

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(7) The compound $CClF_2N{=}NCF_3$ was recently described by V. A. Ginsburgh, A. Ya. Yakubovich, A. S. Filatove, V. A. Shpanskii, E. S. Vlasova, G. E. Zelenin, L. F. Sergienko, L. L. Marlynova, and S. P. Makarov, *Dokl. Akad. Nauk SSR*, **142**, 88 (1962). These workers reported an observed boiling point of 4.5°.

cipal products.[8,9] Therefore, the low-temperature reaction of ClCN with AgF_2 was attempted in order to determine whether or not products such as the corresponding azo compound $CClF_2N{=}NCClF_2$ could be obtained in this manner. Accordingly, when a mixture of ClCN and AgF_2 contained in a steel cylinder at −196° was rocked and allowed to warm very slowly to room temperature, a vigorous reaction occurred which produced a very complex product which has not as yet been resolved. It was observed however, that the dilution of such a mixture with elemental chlorine greatly reduced the vigor of this reaction leading to a more tractable product. When ClCN mixed with chlorine was condensed into the cylinder containing an excess of AgF_2 and the mixture warmed under autogenous pressure as before, the product could readily be separated into portions which were resolved chromatographically. There were formed, in addition to the expected CF_4, $CClF_3$, $CF_3N{=}NCF_3$, CCl_2F_2, and CCl_3F, the unsymmetrical azo compound $CClF_2N{=}NCF_3$ already described and the interesting substance CF_3NCl_2, which constituted the greater part of the portion condensed at −80°. It was also found that when the molar ratio of chlorine to cyanogen chloride was raised from approximately 1:6 to 2:1, the yield of CF_3NCl_2 produced was increased from 10 to 30 ± 5%, while the proportions of the corresponding azo compounds formed were markedly reduced. Pure CF_3NCl_2 is a faintly yellow liquid, bp 14.9°, mol wt 157 (calcd 154). It is interesting to note that no appreciable amounts of the symmetrical azo compound $CClF_2N{=}NCClF_2$ were detected under any of the conditions employed.

The photolysis of CF_3NClF and of CF_3NCl_2 alone or in the presence of CO has been shown to proceed in accordance with the equations

$$CF_3NClF \xrightarrow{h\nu} CF_3N{=}NCF_3 + [ClF]$$

$$CF_3NCl_2 \xrightarrow{h\nu} CF_3N{=}NCF_3 + Cl_2$$

$$CF_3NCl_2 + CO \xrightarrow{h\nu} CF_3N{=}NCF_3 + COCl_2$$

Also, these compounds readily oxidized KI solution, and the CF_3NCl_2, which is fairly stable to dilute alkali, has been stored in glass for 6 months with only slight change. These facts are in full accord with the structures of the compounds. Finally, it may be noted that the nitrene, CF_3N:, which was presumably an intermediate in the photolyses, always dimerized and that, even in the presence of an excess of CO or O_2, neither CF_3NCO nor CF_3NO was formed.

Experimental Section

Apparatus and Materials.—The direct fluorinations were operated in a single-jet, single-stage reactor, 21 in. in length and equipped with a $^1/_{16}$-in. stainless steel jet. The reactant was metered from a stainless steel cylinder, diluted with nitrogen, carried directly into the jet, and treated with undiluted fluorine in the usual manner. The remaining equipment and operating conditions were essentially identical with those which have been described previously.[3] The indirect fluorinations were carried out under pressure in a 300-cc Hoke stainless steel cylinder equipped with a valve and a pressure gauge except as otherwise indicated.

Chromatographic separations were made with a Micro-Tek 1500 chromatograph using Kel-F no. 3 polymer oil (33%) on Chromosorb-P (60–80 mesh) in all columns except as otherwise indicated. Analytical separations were made using a column 15 ft × 0.25 in. o.d., and semipreparative separations were made mostly with a column 15 ft × 0.375 in. o.d., both usually operated at ambient temperature. Infrared absorption spectra were measured with a Beckman IR-8 spectrophotometer, while the ultraviolet spectra were examined using a Beckman DB spectrophotometer.

Elemental fluorine was supplied in cylinders by the General Chemical Division, Allied Chemical Corp., and was passed over sodium fluoride pellets before being metered into the reactor. The argentic fluoride was freshly prepared by the exhaustive fluorination of argentous fluoride at 250°, while the cyanogen chloride was synthesized according to the established procedure.[10]

The Direct Fluorination of ClCN.—This compound (19 g), at the flow rate of 0.032 mole/hr, was fluorinated in the single-jet, single-stage reactor at the molar reaction ratio (F_2:sample:N_2) of 5.3:1:10, at 94° for 9 hr and yielded 20 ml of crude product. At first this untreated crude product was separated by rectification into four portions: I, bp −114 to −98°, mol wt 88–90 (2 cc); II, bp −88 to −45°, mol wt 105–108 (3 cc); III, bp −35 to 0°, mol wt 105–130 (8 cc); and IV, residue (7 ml). Vaporized samples of each of these portions were then analyzed by chromatography and infrared spectroscopy, the total yields being estimated from chromatographic peak areas and based upon the quantity of ClCN consumed, together with the estimated or previously measured densities of the several components.[3] There were formed the known CF_4 (trace), $CClF_3$ (15%), Cl_2 (12%), $CF_3N{=}NCF_3$ (10%), and CCl_2F_2 (5%) together with three new compounds later identified as $CClF_2NF_2$ (10%), CF_3NClF (12%), and $CClF_2N{=}NCF_3$ (15%) and with an unidentified residue (6%).

Later fraction III was passed through 10% aqueous NaOH, dried over $CaSO_4$, and then resolved by semipreparative chromatography using a special 6 ft × 0.375 in. o.d. column, packed with Florosil and maintained at 15°. The first compound eluted from the column, immediately preceding $CF_3N{=}NCF_3$, was $CClF_2NF_2$, a colorless, stable gas, mol wt (effusion method)[11] 137 ± 2 (calcd 137.5), isolated in small quantity only, since it was just barely resolved by this column. Its infrared spectrum, which indicated no unsaturation, showed absorptions at 1225 (s), 1174 (s), 1107 (m), 1066 (m), 980–952 (s) (complex), and 927 (m) cm^{-1}. The mass spectrum (see Table I) was completely consistent with the assigned structure, while the F^{19} nmr spectrum exhibited two peaks at −104.3 ppm (NF_2) and −14.5 ppm ($CClF_2$), referred to CF_3COOH, with relative areas in the ratio of 1.1:1.

The next new product had a retention time only slightly greater than $CF_3N{=}NCF_3$. This was CF_3NClF, a stable, colorless gas, bp (extrapolated) −32.8°, mol wt 139 (calcd 137.5). Its infrared spectrum, which indicated no unsaturation, showed absorptions at 1258 (s), 1205 (s), 937 (m), 876 (m), and 741 (m) cm^{-1}. Its gas-phase ultraviolet spectrum exhibited a maximum at 238 $m\mu$, while the mass spectrum (see Table I) was consistent with the proposed structure. The F^{19} nmr spectrum exhibited two peaks at −68.6 ppm (NClF) and +3.0 ppm (CF_3), referred to CF_3COOH, with relative areas in the ratio of 1:2.8.

Then fraction IV was passed through 10% aqueous NaOH to remove unreacted ClCN, dried, and chromatographed on the Kel-F column. It was shown to contain only one major component, namely, $CClF_2N{=}NCF_3$, which was a yellow liquid, bp

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5.8° (extrapolated), mol wt 180 (calcd 182.5), $\Delta H_{\text{vap}} = 5.86$ kcal/mole, and Trouton's constant = 21.0 cal/deg mole. Its infrared spectrum showed absorptions at 1227 (s, b), 1163 (m), 1064 (m), 1014 (m), 943 (w), 800 (m), and 702 (m) cm^{-1}. The ultraviolet spectrum exhibited a maximum at 372 mμ, indicating the presence of an azo linkage. The F^{19} nmr spectrum showed two absorptions at −21.2 ppm ($CClF_2$) and −1.0 ppm (CF_3), referred to CF_3COOH, with relative areas in the ratio of 2.0:3.2.

The Indirect Fluorination of ClCN by AgF_2 in the Presence of Chlorine.—Approximately 30 g (0.4 mole) of ClCN and 6 g (0.08 mole) of chlorine were condensed onto 180 g (1.2 mole) of AgF_2 in the 300-cc steel cylinder at −196°. After evacuation, the bomb was closed, wrapped in glass wool, placed in an open brass cylinder, and rocked while warming gradually to room temperature. After 20 hr the contents of the cylinder was passed under reduced pressure through a series of glass traps maintained at −80, −126, and −196°, respectively. The coldest trap contained 6 ml of material which was shown by chromatography and infrared analysis to consist of CF_4, $CClF_3$, and $CF_3N{=}NCF_3$. The trap at −126° had collected 13 ml of crude product, which was passed through 10% aqueous NaOH to remove free chlorine, after which 5 ml of dried product was recovered. A completely vaporized sample of this was then analyzed by chromatography and infrared spectrum and shown to contain $CF_3N{=}NCF_3$ (40%), CCl_2F_2 (15%), and CCl_3F (15%), together with CF_3NCl_2 (15%) and $CClF_2N{=}NCF_3$ (13%) (see above). Percentages were calculated on the basis of chromatographic peak areas, assuming, as usual, equal thermal conductivities for all components. The trap at −80° (3 ml) contained three components which were separated in the manner just described. They were $CClF_2N{=}NCF_3$ (25%), CF_3NCl_2 (50%), and CCl_3F (25%). The over-all yield of CF_3NCl_2 was approximately 10%.

A second experiment designed to favor the formation of the dichloramine by increasing the Cl_2 concentration was conducted in a 75-cc stainless steel bomb. This was first charged with 7.3 g (0.05 mole) of AgF_2 and after evacuation 3.1 g (0.05 mole) of ClCN and 7.8 g (0.11 mole) of Cl_2 were condensed in successively. The vessel was then allowed to warm slowly to room temperature while being rocked and finally left to stand at room temperature for 2 days. Analysis of the crude product by the method outlined above showed that the major constituent boiling above −30° was CF_3NCl_2, which was obtained in an estimated yield of 30 ± 5%. The corresponding amounts of the two azo compounds $CF_3N{=}NCF_3$ and $CClF_2N{=}NCF_3$ had been markedly reduced, as expected.

Pure CF_3NCl_2 (2 ml) was isolated by repetitive chromatography on the Kel-F column. It was a faintly yellow liquid, bp 14.9° (extrapolated), mol wt 157 by gas density (calcd 154), $\Delta H_{\text{vap}} = 6.1$ kcal/mole, and Trouton's constant = 21.3 cal/deg mole. Its infrared spectrum showed major absorptions at 1399 (w), 1250 and 1229 (s), 1188 (s), 895 (w), 806 (m), and 704 (m) cm^{-1}. The vapor-phase ultraviolet spectrum exhibited a single maximum centered at 287 mμ (NCl_2). The mass spectrum exhibited the following principal *m/e* values in order of decreasing relative intensity (Cl^{37} ions omitted): 69 (CF_3^+), 99 ($CClF_2N^+$), 70 (Cl_2^+), 80 ($CClFN^+$), 49 (NCl^+), 31 (CF^+), 35 (Cl^+), 64 (CF_2N^+), 153 ($CCl_2F_3N^+$) (parent ion), 45 (CFN^+), 118 ($CClF_3N^+$), and 50 (CF_2^+). The F^{19} nmr spectrum showed only one peak at −19.4 ppm (CF_3), relative to CF_3COOH. This compound readily oxidized neutral KI solution, was fairly stable toward dilute alkali, and has been stored in glass for 6 months at ambient temperature with only slight decomposition.

One fluorination of ClCN by AgF_2 in the absence of chlorine has been run. The reaction appeared to be much more vigorous than when chlorine was present and yielded a highly complex mixture of products which has not as yet been resolved, but no CF_3NCl_2 was formed.

Ultraviolet Irradiations.—These reactions were conducted in a Monel infrared gas cell, 10 cm in length and equipped with NaCl windows. The source employed was a 550-w high-pressure Hg lamp.

When the cell had been pressurized with 50 mm of CF_3NCl_2 and irradiated for 15 min, most of the reactant was consumed. The major products were $CF_3N{=}NCF_3$, identified by its infrared spectrum and chromatographic retention time, and Cl_2, identified by its chromatographic retention time, lack of any infrared absorptions, and its reaction with water followed by precipitation with $AgNO_3$. Traces of N_2O and COF_2 were also detected by infrared analysis.

When CF_3NCl_2 (at 50 mm) was mixed with an excess of CO (at 700 mm) and the mixture photolyzed for 10 min, the products were $CF_3N{=}NCF_3$ and $COCl_2$ together with traces of COF_2, the latter two compounds being identified by infrared, but no CF_3NCO was detected. In an analogous experiment in which O_2 (at 700 mm) was substituted for the CO, the products were $CF_3N{=}NCF_3$ and traces of COF_2, but no CF_3NO was produced.

The irradiation of CF_3NClF under analogous conditions proceeded somewhat more slowly than that of the dichloramine and after 0.5 hr produced $CF_3N{=}NCF_3$, together with COF_2, N_2O, and CO_2. The NaCl windows were badly attacked during this reaction, indicating the presence of a reactive intermediate such as ClF.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation of Hexathiocyanatorhenium(IV) Ion by a Fused-Salt Reaction[1]

BY R. A. BAILEY AND S. L. KOZAK

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A number of reports of rhenium thiocyanate complexes may be found in the literature. Most of these are prepared by the reduction of a perrhenate and apparently contain coordinated oxygens. They are generally not well characterized. Nelson and Boyd[2] have described the magnetic properties of a series of Re(IV) hexathiocyanates but have given no method for their preparation or analytical results. In fact, no other reference to these compounds can be found in the literature.[3] In view of this, we have taken advantage of the reactivity of molten salts to prepare compounds of $[Re(SCN)_6]^{2-}$ from K_2ReCl_6.

Experimental Section

K_2ReCl_6 was prepared by the method of Rulfs and Meyer.[4] All other chemicals were reagent grade.

The preparation was carried out in a large stoppered test tube which was surrounded by a cylindrical furnace. An electronic

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