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THE REACTIONS OF IMINOSULFUR DIFLUORIDES AND CHLORINE MONOFLUORIDE

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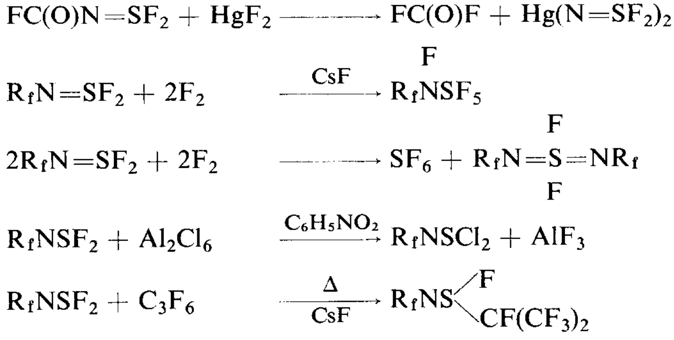
SUMMARY

The reactions of perfluoroalkyl- and perfluoroacyl-iminosulfur difluorides with chlorine monofluoride result in the preparation of perfluoroalkyldichloroamines and a new class of componds *N,N*-dichloroperfluoroamides, $R_fC(O)NCl_2$, *via* the elimination of SF_4. The amides, $FC(O)NCl_2$ and $CF_3C(O)NCl_2$, in addition to 1,2-bis-(dichloroamino)tetrafluoroethane, $Cl_2NCF_2CF_2NCl_2$, are reported and characterized. The reactions of ClF with other sulfur(IV) imines proceed in an analogous manner to form perfluoroalkyl-dichloroamines *via* the elimination of the corresponding sulfur(IV) fluoride.

INTRODUCTION

The chemistry of the class of compounds $RNSF_2$ has primarily been concerned with sulfur–fluorine reactions, carbon–nitrogen bond cleavage and sulfur–nitrogen double bond cleavage or saturation with concommitant oxidation of sulfur(IV) to sulfur(VI)[1,2].



$$FC(O)N{=}SF_2 + HgF_2 \longrightarrow FC(O)F + Hg(N{=}SF_2)_2$$

$$R_fN{=}SF_2 + 2F_2 \xrightarrow{CsF} R_f\overset{F}{N}SF_5$$

$$2R_fN{=}SF_2 + 2F_2 \longrightarrow SF_6 + R_fN{=}\overset{F}{\underset{F}{S}}{=}NR_f$$

$$R_fNSF_2 + Al_2Cl_6 \xrightarrow{C_6H_5NO_2} R_fNSCl_2 + AlF_3$$

$$R_fNSF_2 + C_3F_6 \xrightarrow[CsF]{\Delta} R_fNS\begin{matrix}\diagup F \\ \diagdown CF(CF_3)_2\end{matrix}$$

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Of the reaction types, the chemistry of the sulfur–nitrogen double bond has been the least studied. In an attempt to learn more about the chemistry of this bond, the reactions of perfluoroacyl- and perfluoroalkyl-iminosulfur difluorides with ClF were investigated.

RESULTS AND DISCUSSION

Perfluoroacyliminosulfur difluorides react *via* the elimination of SF_4 and the formation of the corresponding *N,N*-dichloroperfluoroamides

$$R_fC(O)NSF_2 + ClF \rightarrow R_fC(O)NCl_2 + SF_4$$
$$R_f = F, CF_3$$

In contrast, $FC(O)NSF_2$ did not react when excess Cl_2 was substituted for ClF. When equal amounts of F_2 and $FC(O)NSF_2$ were mixed at −78° relatively little reaction occurred, while at 23° conversion to nitrogen, COF_2 and SF_6 took place. Based on the products formed and the polar nature of ClF[3, 4], the polarization of the nitrogen–sulfur bond is $N^{\delta-}—S^{\delta+}$. To ensure that this effect is not a result of the carbonyl function, ClF was shown to react analogously with perfluoroalkyliminosulfur difluorides.

$$R_fNSF_2 + ClF\ (\text{excess}) \rightarrow R_fNCl_2 + SF_4$$
$$R_f = CF_3,\ i\text{-}C_3F_7,\ F_2NSCF_2CF_2$$

An infrared analysis of substituted NSF_2-containing compounds[5] has been interpreted as involving the nitrogen lone-pair electrons in p_π–d_π bonding with sulfur to increase the NS bond order and thus account for the seemingly high value for the N=S stretching frequency. As a result of this p_π–d_π bonding, a canonical structure of the form $R\overset{+}{N}\equiv\overset{-}{S}F_2$ was suggested. Although the argument presented favoring this structure seems reasonable, the reactions of ClF and perfluoroacyl- and perfluoroalkyl-iminosulfur difluorides do not support this type of polarization. The observed mode of reactivity may be explained by an induced positive charge on sulfur due to the electron-withdrawing effect of the fluorines. Alternatively, considering the possible *cis* and *trans* rotational isomers of the $RNSF_2$ compounds[6], the *trans* orientation would facilitate electrophilic attack at the less sterically-hindered nitrogen lone-pair.

The iminosulfur difluorides apparently react with ClF in a manner analogous to perfluorinated nitriles[3]. However, when attempts were made to isolate the intermediate product, $R_f\overset{Cl}{N}—SF_3$, by altering the stoichiometry of the reactants, the reaction still proceeded to form the corresponding *N,N*-dichloro derivative leaving unreacted starting material. This can be explained in part on the basis of the relatively weak N—S bond which could cleave readily. Since the N—Cl bond is polarized $N^{\delta-}—Cl^{\delta+}$, the nitrogen should be more susceptible to electrophilic attack by $Cl^{\delta+}$ than the S=N or C≡N bond, thereby accounting for the greater reactivity of the monosubstituted product over the parent, and precluding isolation of the former.

The formation of *N*,*N*-dichloro derivatives with ClF from the $-N-S\lessdot$ system was found to be a general reaction for other sulfur–nitrogen derivatives. The reactions of *N*,*N*′-perfluoroisopropylsulfur di-imide [7] and *N*-sulfinyl trifluoromethylamine* also proceed with the formation of *N*,*N*-dichloroperfluoroalkylamines by the elimination of the sulfur(IV) fluoride.

$$\begin{aligned} &CF_3NSO + ClF \text{ (excess)} \rightarrow CF_3NCl_2 + SOF_2 \\ &(i\text{-}C_3F_7N{=})_2S + ClF \rightarrow i\text{-}C_3F_7NCl_2 + SF_4 \end{aligned}$$

There were, however, some cases in which SF_4 was eliminated from iminosulfur difluorides but the corresponding *N*,*N*-dichloro compounds were not isolated. The reactions of ClF with $ClNSF_2$, $NCNSF_2$ and $(F_2SN)_2CF_2$ resulted in the elimination of SF_4 but also gave considerable amounts of N_2 and Cl_2. In the reaction of $ClNSF_2$, nitrogen was formed quantitatively as determined by mass spectrometry and *PVT* measurements. The yield of SF_4, freed from chlorine by reaction with mercury, was also nearly quantitative. These products were not totally unexpected due to the unstable nature of the expected product NCl_3. In the case of $NCNSF_2$ or $(F_2SN)_2CF_2$, CF_3NCl_2 was the only isolated dichloroamine. We had anticipated that these reactions would result in the preparation of $(Cl_2N)_2CF_2$ since both functional groups react with ClF to generate NCl_2 derivatives. If the iminosulfur difluorides are used in excess and the reaction time decreased, the only isolated dichloroamine was again CF_3NCl_2. This seems to indicate that the rate of formation of CF_3NCl_2 from ClF and the intermediate monosubstituted or disubstituted product is faster than the rate at which the intermediate is produced. The decomposition products indicate that NCl_3, which could form at one of several steps, is an intermediate in the decomposition.

N,*N*-Dichlorofluoroformamide and *N*,*N*-dichlorotrifluoroacetamide are the first members of the new class of compounds *N*,*N*-dichloroperfluoroamides, $R_fC(O)NCl_2$. The unfluorinated analogs are reported to be unstable[8], *viz.*, $HC(O)NCl_2$ explodes above 0°, and $CH_3C(O)NCl_2$ decomposes on standing at room temperature. In contrast, the fluorinated derivatives can be quantitatively recovered after heating in Pyrex glass for 24 h at 125°, and are not sensitive to shock under ordinary handling. Both compounds freeze to nearly white solids and melt to give volatile light-yellow liquids. Although the totally fluorinated amides[9], $R_fC(O)NF_2$, are sensitive to moist air, brief exposure under similar conditions did not result in any decomposition of the chlorinated molecules.

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* During the preparation of this manuscript the reaction of FSO_2NSO and ClF was described (H. W. Roesky, *Angew. Chem. Intern. Edn.*, *10* (1971) 265).

1,2-Bis-(dichloroamino)tetrafluoroethane exhibits similar properties. Although it has little vapor pressure at room temperature, it transfers very slowly under static vacuum. The previous method of preparing perfluoroalkyldichloroamines involves the reaction of the corresponding perfluoroalkylnitrile with ClF[3]. This is superior for some derivatives because it eliminates the need of preparing the iminosulfur difluoride intermediate, but it lacks the general applicability of the route described here. The use of the nitrile function results in the dichloroamine group being bonded to a CF_2 group

$$R_fCN + ClF \rightarrow R_fCF_2NCl_2$$

The iminosulfur difluoride group adds to alkenes *via* photolytic or thermal reactions of the *N*-chloro and *N*-bromo derivatives[10,11] or forms from amides, amines or imines by using SF_4[1,2]. From these intermediates, using ClF, the NCl_2 group can be introduced on a more substituted carbon, *e.g.*,

$$(CF_3)_2CFNSF_2 + ClF\ (\text{excess}) \rightarrow (CF_3)_2CFNCl_2$$

In general, attempts to fluorinate the NCl_2 group with metal fluorides resulted in decomposition of the compound. Thus, when $FC(O)NCl_2$ was reacted with HgF_2 at room temperature or with KF at −20°, COF_2 and nitrogen were formed. With CsF at 130°, $Cl_2NCF_2CF_2NCl_2$ gave $C_2F_5NCl_2$ as the major dichloroamine product in addition to nitrogen. Reactions to form metal chlorides by using HgO, AgO or Ag_2O likewise resulted in slight decomposition of $FC(O)NCl_2$ to COF_2 and nitrogen, while with $Cl_2NCF_2CF_2NCl_2$ virtually no reaction occurred.

Chlorinating agents, such as PCl_3, PCl_5 or Al_2Cl_6, did not displace the fluorine from the carbonyl moiety but rather the reactions resulted in the liberation of chlorine gas and the formation of a solid or viscous non-volatile liquid. The volatile gases contained no infrared active molecules indicating complete consumption of the dichloroamide. These reactions and the lack of reactivity toward silver and mercury salts support the polarization of the NCl bond as $N^{\delta-}$—$Cl^{\delta+}$.

The photolyses of *N,N*-dichloroperfluoroamines give azo compounds[12] presumably *via* the coupling of the corresponding nitrene. When $FC(O)NCl_2$ or $CF_3C(O)NCl_2$ was photolyzed at 3000 Å we were unable to isolate either the corresponding azo compound or the isocyanate which would support the presence of the nitrene intermediate in the perfluoroalkyl derivatives. Cleavage resulted to give COF_2 and COFCl, or CF_3Cl and $COCl_2$, plus CO and N_2. Photolysis of $Cl_2NCF_2CF_2NCl_2$ yelded nitrogen, chlorine and a non-volatile, presumably polymeric, material. An ^{19}F NMR of this material showed mainly one resonance at $\varphi = 109$. A mass spectrum was not helpful in determining the structure since substantial cleavage occurred and chlorine clusters were also found.

The reactions of compounds of the type $XCCl_2NF_2$ with mercury generate *N*-fluoroimines in good yields and do not undergo complete dechlorofluorination to produce substituted nitriles[13]. In contrast, we have found that $Cl_2NCF_2CF_2NCl_2$ is dechlorofluorinated to yield cyanogen quantitatively in 0.5 h at 25°. Reduction of the reaction time to approximately one minute still resulted in cyanogen formation, but infrared and NMR spectra gave some evidence for the presence of trace amounts of a material which contains an imine function. However, after several one minute runs, insufficient amounts of any imine could be isolated for identification.

Spectral and physical data for $FC(O)NCl_2$, $CF_3C(O)NCl_2$ and $Cl_2NCF_2CF_2NCl_2$ are given in Table 1. The ^{19}F NMR resonances are found in the expected regions for these derivatives and show no splitting due to nitrogen. The infrared and mass spectra are also consistent with the proposed structures. The carbonyl stretching frequencies at 1853 and 1775 cm^{-1} show a shift to lower energy compared to the *N*,*N*-difluoro derivatives[9,14]. The C—F stretching frequencies and deformations are readily assigned to bands between 1050 and 1300 cm^{-1} and 720 to 740 cm^{-1}, respectively. The low intensity of the N—Cl absorption band prevents definite assignment in $CF_3C(O)NCl_2$ and $Cl_2NCF_2CF_2NCl_2$, but the band at 680 cm^{-1} in $FC(O)NCl_2$ is in the correct region for this stretching mode.

Chlorine monofluoride does not react analogously with sulfur(VI) imines. The interaction of $FC(O)NS(O)F_2$ with ClF does not give $FC(O)NCl_2$, although SOF_4 was formed. At −78° little reaction occurred after 4 h, while at 25° there was a 90% conversion to COF_2 and SOF_4 based on the recovered starting material. The decomposition of 2 mmole of $FC(O)NCl_2$ by reaction with an equal amount of ClF to give COF_2, N_2 and Cl_2 was 10–20% at −78° (4 h) and 50% at 23° (3 h). This suggests that $FC(O)NCl_2$ is not an intermediate in the $FC(O)NS(O)F_2$–ClF reaction. This result may be explained by an initial attack at the C—N bond because of the stronger N=S bond and the relative inertness of the sulfur(VI) derivatives.

EXPERIMENTAL

Starting Materials

Chlorine monofluoride was purchased from Ozark–Mahoning Co., SF_4 from K & K Laboratories, Inc., $(CN)_2$ from Matheson Co., Inc. and $CF_3C(O)NH_2$ from Aldrich Chemical Co., Inc. The cesium fluoride (American Potash & Chemical Corp.) was dried *in vacuo* at 170°, $KF{\bullet}2H_2O$ (J. T. Baker Chemical Co.) was dehydrated at 300° and anhydrous NaF (Baker & Adamson) was used as received. The iminosulfur difluorides, $FC(O)NSF_2$[15], $CF_3C(O)NSF_2$[16], CF_3NSF_2[6], $i\text{-}C_3F_7NSF_2$[17], $NCNSF_2$[18], $ClNSF_2$[19], $(F_2SN)_2CF_2$[20], in addition to $FC(O)NS(O)F_2$[19], were prepared from the literature methods. The synthesis of $F_2SNCF_2CF_2NSF_2$ was accomplished by modifying the CF_3NSF_2 preparation and using $(CN)_2$, SF_4 and CsF at 155° for 3 h. The compound CF_3NSO was made from CF_3NSCl_2[21] and red HgO (J. T. Baker Chemical Co.) without solvent.

TABLE I

SPECTRAL AND PHYSICAL DATA

		$FC(O)NCl_2$ (nc)	$CF_3C(O)NCl_2$ (nc)	$Cl_2NCF_2CF_2NCl_2$ (nc)
IR (cm^{-1})		1853(vs), 1232(vs), 1200(sh,ms) 990(mw), 890(mw), 740(pqr,mw) 680(mw)	1770(vs), 1305(m), 1238(vs) 1195(vs), 1136(vs), 820(vw) 719(m)	1285(mw), 1205(vs), 1135(vs) 1050(vs), 1027(sh,mw), 825(w) 730(mw)
^{19}F (ppm)*		17.7(s)	67.8(s)	92.3(s)
Analysis **	C	9.04 (9.11)	13.39 (13.20)	9.04 (8.90)
	N	10.42 (10.62)	7.53 (7.70)	10.28 (10.38)
	Cl	53.62 (53.75)	38.78 (38.97)	52.42 (52.55)
	F	14.5 (14.4)	31.2 (31.33)	27.9 (28.16)
Mol. wt.**		128.6 (131.9)	179 (181.9)	—
$\log P_{mm} = a - b/T$				
a		9.06	8.89	8.14
b		2125.7	2136.1	2248.5
b.p.(°C)		71	82 ± 1	154
ΔH_{vap} (kcal/mol)		9.73	9.77	10.3
ΔS_{vap} (e.u.)		28.3	27.5	24.1

* From $CFCl_3$ internal standard.

** Calculated values in parentheses.

Apparatus

Volatile liquids and gaseous materials were handled in a standard Pyrex vacuum line equipped with a Heise–Bourdon tube gauge. The reactions were carried out in 30 ml or 75 ml Hoke bombs, and product separation was accomplished *via* fractional condensation. In general, one separation afforded an analytically pure sample.

Analysis

Infrared spectra were taken on a Perkin–Elmer 457 spectrometer using a 10 cm Pyrex glass cell with KBr windows. The ^{19}F NMR spectra were obtained on a Varian Model HA-100 spectrometer operating at 94.1 mHz. Mass spectra were obtained with a Hitachi Perkin–Elmer RMU-6E mass spectrometer at 17 and 70 eV. Elemental analyses were obtained from Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

General Procedure

In a typical run, 3–6 mmole of the appropriate —NSF_2 compound was condensed into a 30 ml Hoke bomb followed by ClF in slight excess of 2:1. After reacting at 23° or below, the volatiles were condensed into a U-trap cooled at —196° and the non-condensables pumped out. As the amount of non-condensables increased, the product yields were found to decrease, and attempts to scale-up the reactions to 10–15 mmole generally resulted in decreased yields. The reaction conditions and yields are summarized in Table 2.

The identification of CF_3NCl_2[12] and i-$C_3F_7NCl_2$[7] was accomplished by comparison of their infrared spectra, and their purity determined by ^{19}F NMR spectroscopy.

TABLE 2

EXPERIMENTAL CONDITIONS

Reactant	Product	Reaction Temp./ Time	Fractionation Temperature (°C) *	% Yield
$FC(O)NSF_2$	$FC(O)NCl_2$	—78°/4 h	-45, $-\underline{78}$, -196	90
$CF_3C(O)NSF_2$	$CF_3C(O)NCl_2$	23°/2 h	$-\underline{45}$, $-\underline{63}$, -196	80
$F_2SNCF_2CF_2NSF_2$	$Cl_2NCF_2CF_2NCl_2$**	23°/4 h	$-\underline{20}$, $-\underline{45}$, -196	58
CF_3NSF_2	CF_3NCl_2	—78°/4 h	-78, $-\underline{98}$, -196	60
i-$C_3F_7NSF_2$	i-$C_3F_7NCl_2$	—78°/4 h	-45, $-\underline{78}$, -196	72
$FC(O)NS(O)F_2$	N_2, COF_2, SOF_4, Cl_2	23°/6 h	— — —	—
CF_3NSO	CF_3NCl_2	—78°/3 h	-78, $-\underline{98}$, -196	60

* Product was isolated at temperature underlined.

** 4:1 excess of ClF. The direct reaction of ClF and $(CN)_2$ under the same conditions gives higher yields.

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