Photolysis of Tetrafluorohydrazine and Thiocarbonyl Chloride. Preparation of Dichlorodifluoraminomethanesulfenyl Chloride and Some Polyhalodifluoraminomethanes[1]

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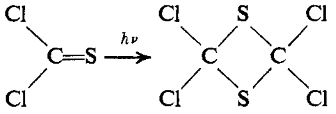
Abstract: Photolysis of N_2F_4 and $CSCl_2$ produces a variety of products, including NF_2Cl_2CSCl, NF_2CCl_3, and NF_2CFCl_2. The yields of NF_2Cl_2CSCl and NF_2CCl_3 are strongly influenced by reaction conditions. NF_2CF_3 can be prepared in good yield by the photolytic reaction of N_2F_4 with $(CF_3)_2CO$. Excess KF with NF_2Cl_2CSCl leads unexpectedly to $CF_3N{=}SF_2$. Thermolysis of NF_2CFCl_2 and mercury gives *syn*- and *anti*-FN=CFCl.

Photolysis reactions of tetrafluorohydrazine and a large number of aromatic hydrocarbons and olefins as well as acetylene lead to saturation by addition of the difluoramino radical.[2] Since other unsaturated systems are likely to behave in an analogous manner, thiophosgene ($CSCl_2$) was selected for study based on the reactivity of the >C=S group in the presence of ultraviolet light, which catalyzes the dimerization of $CSCl_2$ to a white, nonvolatile solid (eq 1).[3]


(1)

A number of products result from irradiating N_2F_4 and $CSCl_2$, including the new sulfur(II) compound dichlorodifluoraminomethanesulfenyl chloride, NF_2Cl_2CSCl. Two other compounds synthesized during this study, trichlorodifluoraminomethane, NF_2CCl_3, and dichlorofluorodifluoraminomethane, NF_2CFCl_2, were revealed while this work was underway.[4a] We have further characterized these new compounds.

Experimental Section

Starting Materials. Thiophosgene (Pfaltz and Bauer, Inc.) was purified by a trap-to-trap distillation. Anhydrous KF was prepared from $KF \cdot 2H_2O$ by dehydrating the salt at 200° for 12 hr in a vacuum oven. Tetrafluorohydrazine (Air Products Co.) and hexafluoroacetone (Pierce Chemicals) were used without further purification.

Caution! Care should be exercised in handling tetrafluorohydrazine since nitrogen–halogen compounds are known to exhibit explosive properties. Any apparatus used should be clean and free of organic materials.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Wallace and Tiernan mechanical gauge. Gaseous starting materials and purified products were measured quantitatively by *PVT* techniques. Photolysis reactions were carried out in a 5-l. Pyrex vessel equipped with a water-cooled quartz probe. For gas chromatographic separations the columns were constructed of 0.25-in. aluminum or copper tubing packed with 20% Kel-F-3 polymer oil (3M Co.) on acid-washed Chromosorb P. In some cases, fractional condensation was used to effect crude separation. Molecular weight measurements were carried out by vapor density techniques with a Pyrex weighing vessel.

Infrared spectra were recorded with a Beckman IR-5A or Perkin-Elmer 621 spectrophotometer by using a 5-cm gas cell equipped with KBr windows or a 10-cm gas cell with AgCl windows. Fluorine-19 nmr spectra were obtained on a Varian HA-100 spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. The ultraviolet light source was a 450-W lamp equipped with a Vycor or Corex filter (Hanovia L-679A36, Engelhard Hanovia, Inc., Engelhard, N. J.).

Preparation of NF_2Cl_2CSCl, NF_2CCl_3, and NF_2CFCl_2. N_2F_4 and $CSCl_2$ were photolyzed under a variety of conditions (Table I) resulting in various yields of the desired compounds. Other products found in these reactions included N_2, *cis*-N_2F_2, NF_2Cl, SiF_4, $(NO)_2SiF_6$, SO_2, SOF_2, S, CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, Cl_3CSCl, CS_2, Cl_2, COS, and $C_2S_2Cl_4$. A crude separation resulted from passing the photolysis products through a series of traps at −47, −78, −120, and −195°. Each trap contained a mixture of products with NF_2Cl_2CSCl stopping at −47°, NF_2CCl_3 at −78°, and NF_2CFCl_2 at −120°. Pure NF_2Cl_2CSCl was obtained by gas chromatography with a 3-ft Kel-F-3 column; NF_2CCl_3 required a 7-ft column, and NF_2CFCl_2 a 24-ft column.

Properties of NF_2Cl_2CSCl. Dichlorodifluoraminomethanesulfenyl chloride is a light yellow liquid at room temperature with an odor similar to that of Cl_3CSCl. It has a vapor pressure of 8 mm at room temperature and reacts slowly with glass but rapidly with mercury. For these reasons a vapor pressure study was not attempted. NF_2Cl_2CSCl gives a single broad peak in the ^{19}F nmr at ϕ −49.9 (CCl_3F internal standard). The infrared spectrum (8 mm of pressure in a 10-cm cell with AgCl windows) is (cm^{-1}): 1013 (m), 923 (m), 895 (s), 873 (s), 844 (s), 775 (w), 628 (m), 541 (m). The principal peaks in the mass spectrum corresponded to the ions S^+, Cl^+, CS^+ (100%), $ClCN^+$, F_2NC^+, SCl^+, $ClCS^+$, $FNCCl^+$, $NCCl_2^+$, F_2NCCl^+, Cl_2CS^+, $FNCCl_2^+$, F_2NClCS^+, $F_2NCCl_2^+$, $FNCl_2CS^+$, Cl_2CSCl^+, $F_2NCl_2CS^+$. Parent peaks ($F_2NCl_2CSCl^+$), although very weak, were noted at mass numbers 201, 203, 205, and 207. NF_2Cl_2CSCl also gave a SiF_3^+ peak resulting from attack on the glass inlet system of the mass spectrometer. All chlorine-containing fragments gave the correct isotopic peaks and relative intensities. Basic hydrolysis of NF_2Cl_2CSCl was used to obtain aqueous solutions for elemental analysis. H_2O_2 was added to the hydrolysis products to oxidize sulfide to sulfate. Fluorine was determined using a specific ion electrode (Orion Research, Inc., Model 94-09). Sulfur and chlorine were both determined gravimetrically as barium sulfate and silver chloride, respectively.

Anal. Calcd for NF_2Cl_2CSCl: S, 15.84; Cl, 52.54; F, 18.75. Found: S, 15.24; Cl, 52.30; F, 18.46.

NF_2Cl_2CSCl + KF. Anhydrous KF was pretreated with hexafluoroacetone (with acetonitrile as solvent) to form the adduct $KOCF(CF_3)_2$ which was thermally decomposed to finely divided

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[1] Presented in part at the Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 1969.

[2] (a) J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967); (b) D. T. Meshri and J. M. Shreeve, *J. Amer. Chem. Soc.*, **90**, 1711 (1968).

[3] H. Tilles, "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, London, 1966, p 311.

[4] (a) V. A. Ginsburg, K. N. Smirnov, and M. N. Vasil'eva, *Zh. Obshch. Khim.*, **39**, 1333 (1969); (b) NF_2CCl_3, bp 41°; (c) NF_2CCl_2F, bp 18°; (d) infrared of NF_2CCl_2F: 1415, 1150, 1042, 925, 910, 725 cm^{-1}.

Table I. Preparation of NF_2Cl_2CSCl, NF_2CCl_3, and NF_2CFCl_2

Reagent					Yield (purified product)		
N_2F_4	$CSCl_2$	Other	Filter	Time[a]	NF_2Cl_2CSCl	NF_2CCl_3	NF_2CFCl_2
10.4[b]	20.0		Corex	3.5	6.2[c]	<5	<5
10.5	29.6		Corex	2	21.6	<5	<5
9.9	29.5		Vycor	2	10.5	<5	<5
7.3	20.5	Cl_2 10.0	Corex	5.4	0	16.7	5
8.6	17.1	Cl_2 8.6	Vycor	2.4	0	15.2	5
10.7	20.2	$SOCl_2$ 13.6	Corex	4	7.9	<5	<5
10.4	20.2	$SOCl_2$ 13.6	Vycor	2	29.4	0	0

[a] Hours. [b] Millimoles. [c] Per cent based on N_2F_4 consumed.

KF and $(CF_3)_2CO$. NF_2Cl_2CSCl (0.61 g, 0.003 mol) and excess KF were allowed to react at room temperature in a 30-ml metal bomb for three days. The volatile products were separated on a 24-ft Kel-F-3 column and the major component was found to be trifluoromethyliminosulfur difluoride (>70% yield). $CF_3N{=}SF_2$ was identified by its infrared spectrum,[6] mass spectrum,[6] molecular weight (calcd, 153.08; found, 152.7), and ^{19}F nmr (CF_3, triplet at 47.97 ppm and SF_2, quartet at −52.01 ppm relative to internal CCl_3F, relative peak areas 2.92:2.0, respectively, J_{F-F} = 10.1 cps).

Properties of NF_2CCl_3. Trichlorodifluoraminomethane exists as a colorless liquid at room temperature and is stable in glass toward mercury up to 55° and is not hydrolyzed by the moisture in the air. Heating NF_2CCl_3 at 110° with mercury for 3 hr resulted in formation of $FN{=}CCl_2$ as the only volatile product. The melting point of NF_2CCl_3 was found to be −21° and a boiling point of 56°[4b] was indicated by the Clausius-Clapeyron equation, $\log P_{mm} = 8.17 - 1740/T°K$. Vapor pressure data are as follows (T, °K; P, mm): 242.5, 10.2; 265.6, 40.5; 273.0, 62.2; 285.3, 115.6; 287.8, 130.0; 297.1, 218.7; 304.5, 300.8; 310.0, 373.8; 311.8, 400.8; 317.0, 485.9; 320.8, 560.2; 324.8, 644.7. The molar heat of vaporization is 7.50 kcal and the Trouton constant is 22.8. The experimental molecular weight was found to be 170.5 (calcd, 170.4). NF_2CCl_3 gives a single broad peak in the ^{19}F nmr at ϕ −50.8. The infrared spectrum (10 mm pressure in a 5-cm cell with KBr windows) is (cm^{-1}): 1024 (m), 912 (s), 884 (vs), 853 (s), 638 (m). The principal peaks in the mass spectrum corresponded to the ions Cl^+, CCl^+, FNC^+, NF_2^+, $FCCl^+$, F_2NC^+, $FNCCl^+$, CCl_2^+, F_2CCl^+, Cl_2CN^+, F_2NCCl^+, $CFCl_2^+$, $FNCCl_2^+$, CCl_3^+ (100%), $F_2NCCl_2^+$, $FNCCl_3^+$. All chlorine-containing fragments gave the correct isotopic peaks and relative intensities.

Properties of NF_2CFCl_2. Dichlorofluorodifluoraminomethane is a colorless gas at room temperature and melts at −96°. NF_2CFCl_2 is not hydrolyzed by the moisture in air but reacts slowly with mercury. The boiling point was found to be 14°[4c] from a Clausius-Clapeyron plot which is described by the equation $\log P_{mm} = 7.80 - 1411/T°K$. Vapor pressure data are as follows (T, °K; P, mm): 209.5, 12.1; 220.8, 25.7; 230.3, 47.6; 237.3, 72.6; 243.0, 99.7; 246.5, 122.6; 252.8, 165.2; 262.0, 261.8; 268.3, 347.1; 273.0, 423.1; 274.3, 448.9; 277.0, 498.3. The molar heat of vaporization is 6.46 kcal and the Trouton constant is 22.5. The experimental molecular weight was found to be 153.4 (calcd, 153.9). Two resonances were observed in the ^{19}F nmr, a triplet (relative areas of 1:1.95:1) at ϕ 55.55 assigned to the CF fluorine and a broad overlapping doublet centered at ϕ −40.45 assigned to the NF_2 group. The relative areas of the NF_2 and CF resonances were found to be 1.93:1 and J_{F-F} = 15.8 cps. The infrared spectrum[4d] (10 mm pressure in a 5-cm cell with KBr windows) is (cm^{-1}): 1147 (s), 1068 (m), 952 (s), 907 (s), 780 (w), 649 (m). The following ions are identified in the mass spectrum: CF^+, NF^+, Cl^+, FCN^+, CCl^+, $ClCN^+$, $FNCF^+$, $FCCl^+$, CF_3^+, $FNCCl^+$, CCl_2^+, $ClCF_2^+$, F_2NCCl^+, $CFCl_2^+$ (100%), $FNCCl_2^+$, F_2NCFCl^+. All chlorine-containing fragments gave the correct isotopic peaks and relative intensities.

NF_2CFCl_2 + Hg. NF_2CFCl_2 (0.20 g, 1.30 mmol) and excess mercury were stirred at 100°, in a 125-cc glass vessel fitted with a Teflon stopcock (Kontes Glass Co.), for 6 hr. The volatile products consisted of $FN{=}CF_2$ (9%), *syn*-$FN{=}CFCl$ (39%) and *anti*-$FN{=}CFCl$ (52%), plus minor amounts of SiF_4, $FN{=}CCl_2$, and unreacted NF_2CFCl_2 (0.14 mmol). The $FN{=}CFCl$ isomers were identified by their infrared and ^{19}F nmr spectra.[7] $FN{=}CF_2$[7] and $FN{=}CCl_2$ were both identified by their infrared spectra.

N_2F_4 + $(CF_3)_2CO$. N_2F_4 (0.457 g, 4.4 mmol) and $(CF_3)_2CO$ (0.73 g, 4.4 mmol) were photolyzed through a Vycor filter until all the tetrafluorohydrazine had reacted. The reaction mixture was passed through traps at −130 and −195°. The −195° trap contained NF_2CF_3 (~57.5% yield) and minor amounts of N_2F_4. The product was identified by its infrared[8] and ^{19}F nmr[9] spectra.

Results and Discussion

As is recorded in Table I, the yield of NF_2Cl_2CSCl formed by the photolysis of N_2F_4 and $CSCl_2$ varies markedly depending upon experimental conditions. $CSCl_2$ decomposes to compounds such as Cl_2, S, CCl_4, and CS_2, and dimerizes according to (1) in the presence of ultraviolet light. Thus, when the molar ratio of $CSCl_2$ to $\cdot NF_2$ is increased by one-half, the yield of NF_2Cl_2CSCl is tripled when a Corex filter is used.

Since NF_2Cl_2CSCl involves an additional atom of chlorine per molecule of product formed, a second source of chlorine radicals should improve the efficiency of the reaction. The addition of elemental chlorine to the reaction mixture precludes the formation of NF_2Cl_2CSCl since chlorination of $CSCl_2$ to form trichloromethanesulfenyl chloride (Cl_3CSCl) occurs rapidly at room temperature.[3] Then Cl_3CSCl apparently reacts with N_2F_4 to form NF_2CCl_3. The best yields of NF_2Cl_2CSCl are obtained when sulfinyl chloride is added to the reaction mixture followed by photolysis using a Vycor filter. Previously, we have concluded that $SOCl_2$ is decomposed slowly to $\cdot Cl$ when photolyzed through Vycor (essentially unaffected if a Corex filter is used).[10] Apparently, under these

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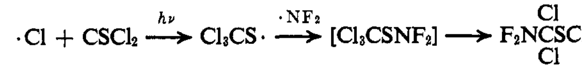
$$\cdot NF_2 + CSCl_2 \xrightarrow{h\nu} F_2N\overset{Cl}{\underset{Cl}{C}}S\cdot \xrightarrow{\cdot Cl} F_2N\overset{Cl}{\underset{Cl}{C}}SCl \qquad (2)$$



$$\cdot Cl + CSCl_2 \xrightarrow{h\nu} Cl_3CS\cdot \xrightarrow{\cdot NF_2} [Cl_3CSNF_2] \longrightarrow F_2N\overset{Cl}{\underset{Cl}{C}}SCl \qquad (3)$$

conditions $SOCl_2$ leads to $\cdot Cl$ which, accompanied by the generated $\cdot NF_2$, results in formation of NF_2Cl_2CSCl at a more rapid rate than Cl_3CSCl which is always found in the product mixture. The effect of the added Cl from $SOCl_2$ is very pronounced when the yield of NF_2Cl_2CSCl is compared with that obtained through Vycor earlier. Formation of NF_2Cl_2CSCl *via* (2) seems a likely route although (3) should be considered. Seel[11] suggested that stepwise fluorination of Cl_3CSCl with KF occurs *via* a Cl_3CSF intermediate, rapidly followed by molecular rearrangement to Cl_2FCSCl until complete fluorination is accomplished. Therefore, (3) seems possible but Cl_3CSNF_2 is never detected. Varying conditions seem to have little effect on the yield of NF_2CCl_2F.

Dichlorodifluoraminomethanesulfenyl chloride is a moderately reactive compound with physical properties which resemble Cl_3CSCl. Identification was made by mass spectrum (peaks assigned to CS^+, SCl^+, $F_2NCCl_2^+$, and $F_2NCl_2CSCl^+$), infrared spectrum (S–Cl stretch at 541 cm^{-1};[12] N–F stretches at 1013 and 895 cm^{-1}), elemental analysis, and ^{19}F nmr. The single broad NF_2 resonance at ϕ −49.9 compares favorably with NF_2CCl_3 at ϕ −50.8. If the other isomer, Cl_3CSNF_2, were formed, the NF_2 resonance would be shifted much farther downfield as in F_3CSNF_2 at ϕ −103.1[13] or even to lower field, as suggested by the data in Table II.

Table II. ^{19}F Nmr of $NF_2CF_xCl_{3-x}$ and $NF_2CF_2CF_xCl_{3-x}$ (x = 0, 1, 2, 3)

Compound	Chemical shifts, ϕ NF$_2$	α-F	β-F	Coupling constants, Hz		
NF_2CF_3[9]	−18.5	84.1			0	
NF_2CF_2Cl[9]	−27.8	62.0			0	
NF_2CFCl_2	−40.5	55.6			15.8	
NF_2CCl_3	−50.8					
a b c				J_{a-b}	J_{a-c}	J_{b-c}
$NF_2CF_2CF_3$[9]	−16.3	119.9	81.8	≈0	10	≈1
$NF_2CF_2CF_2Cl$[9]	−17.9	116.9	69.7	≈0	10.0	2.3
$NF_2CF_2CFCl_2$[9]	−20.7	113.8	72.8	≈0	14.0	7.2
$NF_2CF_2CCl_3$[9]	−27.0	108.0				

When an excess of anhydrous potassium fluoride is allowed to react with NF_2Cl_2CSCl at 25°, the unexpected compound $CF_3N{=}SF_2$ is found to be the major product (>70% yield). This is an unusual rearrangement in that, in addition to fluorination, the nitrogen atom is shifted between the carbon and sulfur. This product is not easily rationalized. However, when N_2F_4 and CF_3SSCF_3 are heated at 225° for 16 hr, $CF_3N{=}SF_2$ is formed.[13]

With the synthesis of NF_2CCl_3 and NF_2CFCl_2, the series $NF_2CF_xCl_{3-x}$ (x = 0, 1, 2, 3) is now complete. As is shown in Table II, when chlorine is successively substituted for fluorine, both the NF_2 and CF resonances are shifted farther downfield. A similar trend is noted in other families, *e.g.*, $NF_2CF_2CF_xCl_{3-x}$ (x = 0, 1, 2, 3), and may be attributed to delocalization of electron density into available d orbitals on chlorine, which deshields the fluorine atoms. The data also indicate that additional chlorine atoms increase the magnitude of spin–spin coupling constants. The NF–CF coupling for NF_2CFCl_2 seems reasonable in light of the increase in J values from $NF_2CF_2CF_2Cl$ to $NF_2CF_2CFCl_2$. The surprisingly large coupling of 15.8 Hz can be explained in terms of a steric effect assuming the major contribution to spin–spin splitting results from direct-through-space interaction.[14]

The volatilities of the compounds NF_2CCl_3 and CCl_4, and NF_2CCl_2F and $CFCl_3$, are similar, and, as the data in Table III show, this holds true for other low molecular weight compounds when an NF_2 group is substituted for chlorine. Also, as the molecular weight of the X group increases, the volatilities of the NF_2 and Cl compounds approach each other. For example, NF_2Cl_2CSCl and Cl_3CSCl both have a vapor pressure of 8 mm at room temperature. Therefore, NF_2 compounds may be expected to be as volatile or slightly more volatile than their chlorine analogs.

Table III. Comparison of Volatility of X–Cl and X–NF_2 Compounds

Compound	Volatility 1 mm	Bp
Cl_3C–Cl	−50°	77°
Cl_3C–NF_2	−60°	56°
Cl_2FC–Cl	−84°	24°
Cl_2FC–NF_2	−92°	19°
$Cl\overset{O}{C}$–Cl	−93°	8°
$Cl\overset{O}{C}$–NF_2	−102°	−5°
NF_2–Cl	−161°	−104°
NF_2–NF_2	−179°	−117°

NF_2CFCl_2 is a useful starting material for the preparation of its imine derivatives by heating with mercury. The reaction is about 50% complete after 1 week at 25°. The products are a 50–50 mixture of *syn*- and *anti*-FN=CClF and traces of FN=CF_2 and FN=CCl_2. After 6 hr at 100°, reaction is nearly complete, with the *anti* form present in slightly larger amounts. This suggests that the *anti* isomer has greater thermodynamic stability, which is surprising, since *cis*-N_2F_2 seems to be the thermodynamically favored form. If the NF_2-

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$CFCl_2$–mercury mixture is heated above 150°, decomposition occurs, with SiF_4 and N_2 the principal volatile products.

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