*Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843, U.S.A.*

The Reaction of Dichloro(difluoramino)methanesulfenyl Chloride with Silver(II) Fluoride

L. M. Zaborowski and Jean'ne M. Shreeve[1]

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Reaction of dichloro(difluoroamino)methanesulfenyl chloride, NF_2CCl_2SCl, with silver(II) fluoride, AgF_2, forms the new compounds, NF_2CCl_2SF and $NF_2CCl_2SF_3$. $NF_2CCl_2S(O)F$ results either from the hydrolysis of $NF_2CCl_2SF_3$ or oxygenation of NF_2CCl_2SF. Hydrogen chloride converts $NF_2CCl_2S(O)F$ to $NF_2CCl_2S(O)Cl$ quantitatively.

Introduction

When dichloro(difluoramino)methanesulfenyl chloride, NF_2CCl_2,SCl, is allowed to react with activated anhydrous potassium fluoride[2] for several days at ambient temperature, complete fluorination, accompanied by molecular rearrangement, to $CF_3N=SF_2$ occurs.[3] While excess KF produces $CF_3N=SF_2$ in 70% yield, a 1:1 molar ratio of KF to NF_2CCl_2SCl results in formation of $CF_3N=SF_2$ and unreacted starting material with no intermediate fluorinated species being isolated. Although no rearrangement is possible, Seel and coworkers showed that complete fluorination of Cl_3CSCl occurs with KF at 150°,[4] and that intermediate fluorinated compounds $CCl_{3-n}F_nSF$ (n = 0–3) were sufficiently stable at −50° to be observed using nuclear magnetic resonance. At room temperature, rapid rearrangement of $CCl_{3-n}F_nSF$ (n = 0–2) to the isomeric sulfenyl chlorides $CCl_{3-n}F_nSCl$ (n = 1–3) takes place. Trichloromethanesulfenyl chloride is completely fluorinated to CF_3SF and its dimer, $CF_3SSF_2CF_3$, by HgF_2 at 130°.[5]

Using AgF_2 as the fluorinating agent with NF_2CCl_2SCl, we have been able to prepare NF_2CCl_2SF which is stable with respect to isomerization and decomposition in metal at room temperature. Furthermore, fluorination of the methylene chlorines does not occur at ambient temperature. Further reaction of the sulfenyl fluoride with AgF_2 results in preparation of the rather easily hydrolyzed sulfur(IV) compound, $NF_2CCl_2SF_3$, which, in the presence of traces of water or of other oxygen-containing species, quickly is converted into the stable sulfinyl compound $NF_2CCl_2S(O)F$. The latter is obtained also in 25% yield by the oxygenation of NF_2CCl_2SF.

$$NF_2CCl_2SF + O_2 \xrightarrow{\text{Pyrex}} NF_2CCl_2S(O)F$$

The reaction of $NF_2CCl_2S(O)F$ with gaseous HCl leads to the quantitative preparation of $NF_2CCl_2S(O)Cl$. Yields of the various products seem to be a function of the AgF_2:NF_2CCl_2SCl ratio with larger amounts of the more highly fluorinated material as the ratio approaches three or greater. Freshly refluorinated AgF_2 gives rise to the most reproducible results.

Experimental Section

Starting Materials. Silver(II) fluoride was prepared by fluorinating AgF (Ozark-Mahoning) in a Monel vessel at 250-300° for 2 hr. Dichloro(difluoramino)methanesulfenyl chloride was obtained from the photolysis of N_2F_4, $CSCl_2$ and $SOCl_2$.[3]

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. For gas chromatographic separations the column was constructed of 0.25 in. aluminum tubing packed with 20% Kel–F–3 polymer oil (3M Co.) on acid-washed Chromosorb P. Molecular weight measurements were carried out by vapor density techniques with a Pyrex weighing vessel.

Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer using a 5 cm gas cell equipped with KBr windows. Fuorine 19 nmr spectra were obtained on a Varian HA-100 spectrometer using trichlorofluoromethane as an internal standard. Mass spectra were run on a Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV.

AgF_2+NF_2CCl_2SCl. In a typical reaction, AgF_2 (5 mmol) was added to a 30 ml Monel vessel. The vessel was evacuated and NF_2CCl_2SCl (2 mmol) condensed in at −195°. After warming, the vessel was maintained at 25° for 6-12 hr. The products, $NF_2CCl_2SF_3$, NF_2CCl_2SF, $NF_2CCl_2S(O)F$, Cl_2, SOF_2, and $FN=CCl_2$, were found in varying yields depending on the condition and relative quantity of AgF_2 used, and the degree of hydrolysis from traces of moisture.

Properties of NF_2CCl_2SF. Dichloro(difluoramino)-methanesulfenyl fluoride is a colorless liquid at 25°.

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[1] Alfred P. Sloan Foundation Fellow.

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The experimental molecular weight was found to be 186.7 (calcd 186.0). Two resonances were observed in the ^{19}F nmr, a triplet (relative areas of 1:1.9:0.9) at φ 270.0 assigned to the SF fluorine and a broad unresolved peak at φ –52.5 attributed to the NF_2 group. The relative areas of the NF_2 and SF resonances were found to be 2.1 and 1 ($J_{F-F}=7.5$ cps). The infrared spectrum (18 torr) is: 1013s, 936s, 906vs, 868s, 840s, 794vs, 630m, 434w cm^{-1}. The following ions are identified in the mass spectrum: $NF_2CCl_2S^+$, Cl_2CSCl^+, $FNCl_2CS^+$, $NF_2CCl_2^+$ Cl_2CSF^+, $FNCCl_2^+$, Cl_2CS^+, NF_2CCl^+, Cl_2CN^+, $ClCSF^+$, NF_2CCl^+, $ClSF^+$, $CClF_2^+$, $FNCCl^+$, F_2CS^+, $ClCS^+$, SF_2^+, SCl^+, CF_3^+, CNF_2^+, FCS^+, $ClCN^+$ (100%), SCN^+, SF^+, SO^+, CCl^+, NS^+, FNC^+, CS^+, HCl^+, Cl^+.

Anal. Calcd for NF_2CCl_2SF: S, 17.2; Cl, 38.1; F, 30.6. Found: S, 16.4; Cl, 38.0; F, 29.5.

Properties of $NF_2CCl_2S(O)F$. Dichloro(difluoramino)methanesulfinyl fluoride is a stable colorless liquid at 25°. Two resonances were found in the ^{19}F nmr, a triplet (relative areas of 1.1:2.0:1.1) at φ 1.3 assigned to the –S(O)F fluorine and a broad unresolved NF_2 resonance at φ –48.1. The relative areas of the NF_2 and –S(O)F peaks were found to be 2 and 1. Due to the close proximity of the –S(O)F and the CCl_3F resonances, SOF_2 was used as the solvent and lock signal to obtain the coupling constant, $J_{F-F}=7.5$ cps. The infrared spectrum (13 torr) is: 1268vs, 1026m, 925s, 890s, 750vs, 638w, 509m, 485vw, 411w cm^{-1}. The following ions were assigned in the mass spectrum: $NF_2CCl_2S(O)F_2^+$, $NF_2CCl_2S(O)F^+$, $NF_2CClFS(O)F^+$, $NF_2CClS(O)F^+$, $FNCClS(O)F^+$, $NF_2CCl_2^+$, $FNCCl_2^+$, $CFCl_2^+$, NF_2CCl^+, Cl_2CN^+, $CClF_2^+$, CCl_2^+, $FNCCl^+$ (100%), SF_2^+, CF_3^+, $CFCl^+$, $S(O)F^+$, NSF^+, NF_2C^+, CSF^+, $ClCN^+$, SCN^+,SF^+, CF_2^+, CCl^+, SO^+, NS^+, FNC^+, CS^+, HCl^+, Cl^+, NF^+.

Anal. Calcd for $NF_2CCl_2S(O)F$: S, 15.87; Cl, 35.11; F, 28.2. Found: S, 15.81; Cl, 35.17; F, 27.9.

$HCl+NF_2CCl_2S(O)F$. $NF_2CCl_2S(O)F$ and excess anhydrous HCl were allowed to react at 25° in Pyrex for 4 hr. The products were passed through a –78° trap which was found to contain pure $NF_2CCl_2S(O)Cl$. Dichloro(difluoramino)methanesulfinyl chloride is a colorless liquid with 5 mm vapor pressure at 25°. The ^{19}F nmr shows a single broad resonance at φ –50.6. The infrared spectrum (4 torr) is: 1257w, 1219s, 1025m, 930m, 914m, 891m, 850vw, 795vw, 635w, 600w, 501m, 455vw. The mass spectrum indicated the following ions: $FNCCl_2S(O)Cl^+$, $NCCl_2SO_2Cl^+$, $NF_2Cl_2CS^+$, $NFCCl_2S^+$, $NF_2CCl_2^+$, $FNCCl_2^+$, NF_2CCl^+, Cl_2CN^+, $CClF_2^+$, CCl_2^+, $SOCl^+$, $FNCCl^+$, CF_3^+, $S(O)F^+$, $CFCl^+$, NSF^+, NF_2C^+. (100%), CSF^+, $ClCN^+$, CF_2^+, SO^+, CCl^+, FNC^+, CS^+, HCl^+, Cl^+.

Results and Discussion

The fluorination and rearrangement of NF_2CCl_2SCl to $CF_3N=SF_2$ in 70% yield[3] when KF is present at ambient temperature led us to investigate the products obtained when another fluorinating agent, *i.e.*, AgF_2, is used under similar conditions. Silver(I) fluoride is found not to react with NF_2CCl_2SCl at 25°.

When the ratio of AgF_2 to NF_2CCl_2SCl is approximately 1.7 and an oxygen-free environment is maintained, NF_2CCl_2SF is obtained in 63% yield. It is thermally stable at 25° in metal but glass attack occurs slowly at room temperature, *e.g.*, it is possible to obtain satisfactory molecular weight data using a Pyrex vessel. In this respect, it resembles i–C_3F_7SF[6] which is formed in a pyrolysis reaction at 200° and which behaves similarly in glass. By contrast, NF_2CCl_2SF is very much unlike its closer analogues, $CCl_{3-n}F_nSF$, which isomerize rapidly at 25°.[4] Heating NF_2CCl_2SF at 100° for one hour in Pyrex results in decomposition to SO_2, $FN=CCl_2$, SiF_4 and minor amounts of $NF_2CCl_2S(O)F$. Excess oxygen and NF_2CCl_2SF in Pyrex at 25° gives SO_2, $FN=CCl_2$, SiF_4 and a 25% yield of $NF_2CCl_2S(O)F$. The high upfield shift of the S–F fluorine (φ 270) is typical of such sulfenyl fluorides, *e.g.*, for FCl_2CSF, φ 265.[4] The mass spectrum does not contain a molecule ion as is observed for the sulfenyl chloride but in the infrared spectrum, a very strong band at 794 cm^{-1} may be assigned to the S–F stretch.

Essentially only infrared evidence is available to support the formation of $NF_2CCl_2SF_3$ which is favored by a greater than 3 fold excess of AgF_2. An infrared spectrum of the product mixture directly from the reaction vessel contained bands, in the S–F region, which are missing in the purified NF_2CCl_2SF and $NF_2CCl_2S(O)F$, and which are reminiscent of those characteristic of CF_3SF_3.[7] Other $-SF_3$ compounds have also been prepared by the fluorination of sulfur(II)-containing species with AgF_2.[8] The presence of $NF_2CCl_2S(O)F$, which is the expected hydrolysis product of $NF_2CCl_2SF_3$ also lends strong support to its preparation in this fluorination reaction.

The quantity of $NF_2CCl_2S(O)F$ obtained varies greatly and is usually low probably due to its subsequent decomposition to $FN=CCl_2$ and SOF_2 catalyzed by unreacted AgF_2 as suggested by the following

$$NF_2CCl_2SCl+AgF_2\rightarrow NF_2CCl_2SF+NF_2CCl_2SF_3$$

$$NF_2CCl_2SF_3\xrightarrow[\text{or MO}]{H_2O}NF_2CCl_2S(O)F$$

$$NF_2CCl_2S(O)F+AgF_2\rightarrow(NF_2CCl_2S(O)F_2)^-+AgF^+ \qquad (1)$$

$$(NF_2CCl_2S(O)F_2)^-\rightarrow(NF_2CCl_2)^-+SOF_2 \qquad (2)$$

$$(NF_2CCl_2)^-\rightarrow FN=CCl_2+F^- \qquad (3)$$

$$AgF+F^-\rightarrow AgF_2 \qquad (4)$$

Therefore, the $NF_2CCl_2S(O)F$ produced is a function of the AgF_2 concentration as well as the presence of traces of H_2O or other oxygen-containing species. Fokin and coworkers[9] suggest that difluoraminocarbanions are unstable with respect to loss of fluoride ion to form a $FN=C<$ imine. Since we also observe imine formation $(FN=CCl_2)$ with AgF_2, and with KF, equations 1-4 may represent a plausible decomposition route.

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Infrared stretching frequency assignments for $-S=O$ can be easily made in both $NF_2CCl_2S(O)F$ and $NF_2CCl_2S(O)Cl$ at 1268 and 1219 cm^{-1} since no other activity is present in this region. These values compare well with the CF_3- analogues, $CF_3S(O)F$, 1268 and $CF_3S(O)Cl$, 1238 cm^{-1}.[7]

Our attempts to understand the differences in the behavior of the $F_nCl_{3-n}CSCl$ system and its close analogues, NF_2CCl_2SCl and CF_3CCl_2SCl, with fluorinating agents are continuing.

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