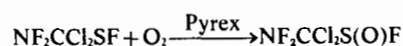


The Reaction of Dichloro(difluoramino)methanesulfonyl Chloride with Silver(II) Fluoride

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Reaction of dichloro(difluoroamino)methanesulfonyl chloride, $\text{NF}_2\text{CCl}_2\text{SCl}$, with silver(II) fluoride, AgF_2 , forms the new compounds, $\text{NF}_2\text{CCl}_2\text{SF}$ and $\text{NF}_2\text{CCl}_2\text{SF}_3$. $\text{NF}_2\text{CCl}_2\text{S(O)F}$ results either from the hydrolysis of $\text{NF}_2\text{CCl}_2\text{SF}_3$ or oxygenation of $\text{NF}_2\text{CCl}_2\text{SF}$. Hydrogen chloride converts $\text{NF}_2\text{CCl}_2\text{S(O)F}$ to $\text{NF}_2\text{CCl}_2\text{S(O)Cl}$ quantitatively.



The reaction of $\text{NF}_2\text{CCl}_2\text{S(O)F}$ with gaseous HCl leads to the quantitative preparation of $\text{NF}_2\text{CCl}_2\text{S(O)Cl}$. Yields of the various products seem to be a function of the $\text{AgF}_2:\text{NF}_2\text{CCl}_2\text{SCl}$ 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.

Introduction

When dichloro(difluoramino)methanesulfonyl chloride, $\text{NF}_2\text{CCl}_2\text{SCl}$, is allowed to react with activated anhydrous potassium fluoride² for several days at ambient temperature, complete fluorination, accompanied by molecular rearrangement, to $\text{CF}_3\text{N}=\text{SF}_2$ occurs.³ While excess KF produces $\text{CF}_3\text{N}=\text{SF}_2$ in 70% yield, a 1:1 molar ratio of KF to $\text{NF}_2\text{CCl}_2\text{SCl}$ results in formation of $\text{CF}_3\text{N}=\text{SF}_2$ and unreacted starting material with no intermediate fluorinated species being isolated. Although no rearrangement is possible, Seel and coworkers showed that complete fluorination of $\text{Cl}_3\text{-CSCl}$ occurs with KF at 150°,⁴ and that intermediate fluorinated compounds $\text{CCl}_{3-n}\text{F}_n\text{SF}$ ($n=0-3$) were sufficiently stable at -50° to be observed using nuclear magnetic resonance. At room temperature, rapid rearrangement of $\text{CCl}_{3-n}\text{F}_n\text{SF}$ ($n=0-2$) to the isomeric sulfonyl chlorides $\text{CCl}_{3-n}\text{F}_n\text{SCl}$ ($n=1-3$) takes place. Trichloromethanesulfonyl chloride is completely fluorinated to CF_3SF and its dimer, $\text{CF}_3\text{SSF}_2\text{CF}_3$, by HgF_2 at 130°.⁵

Using AgF_2 as the fluorinating agent with $\text{NF}_2\text{CCl}_2\text{SCl}$, we have been able to prepare $\text{NF}_2\text{CCl}_2\text{SF}$ 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 sulfonyl fluoride with AgF_2 results in preparation of the rather easily hydrolyzed sulfur(IV) compound, $\text{NF}_2\text{CCl}_2\text{SF}_3$, which, in the presence of traces of water or of other oxygen-containing species, quickly is converted into the stable sulfinyl compound $\text{NF}_2\text{CCl}_2\text{S(O)F}$. The latter is obtained also in 25% yield by the oxygenation of $\text{NF}_2\text{CCl}_2\text{SF}$.

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)methanesulfonyl 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. Fluorine 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.

$\text{AgF}_2 + \text{NF}_2\text{CCl}_2\text{SCl}$. In a typical reaction, AgF_2 (5 mmol) was added to a 30 ml Monel vessel. The vessel was evacuated and $\text{NF}_2\text{CCl}_2\text{SCl}$ (2 mmol) condensed in at -195°. After warming, the vessel was maintained at 25° for 6-12 hr. The products, $\text{NF}_2\text{CCl}_2\text{SF}_3$, $\text{NF}_2\text{CCl}_2\text{SF}$, $\text{NF}_2\text{CCl}_2\text{S(O)F}$, Cl_2 , SOF_2 , and $\text{FN}=\text{CCl}_2$, 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 $\text{NF}_2\text{CCl}_2\text{SF}$. Dichloro(difluoramino)methanesulfonyl fluoride is a colorless liquid at 25°.

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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 ($J_{\text{F-F}}=7.5$ 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: $\text{NF}_2\text{CCl}_2\text{S}^+$, Cl_2CSCl^+ , FNCl_2CS^+ , $\text{NF}_2\text{CCl}_2^+$, 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 $\text{NF}_2\text{CCl}_2\text{SF}$: S, 17.2; Cl, 38.1; F, 30.6. Found: S, 16.4; Cl, 38.0; F, 29.5.

Properties of $\text{NF}_2\text{CCl}_2\text{S(O)F}$. 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_2F resonances, SOF_2 was used as the solvent and lock signal to obtain the coupling constant, $J_{\text{F-F}}=7.5$ 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: $\text{NF}_2\text{CCl}_2\text{S(O)F}_2^+$, $\text{NF}_2\text{CCl}_2\text{S(O)F}^+$, $\text{NF}_2\text{CClF}_2\text{S(O)F}^+$, $\text{NF}_2\text{CClS(O)F}^+$, FNCClS(O)F^+ , $\text{NF}_2\text{CCl}_2^+$, 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 $\text{NF}_2\text{CCl}_2\text{S(O)F}$: S, 15.87; Cl, 35.11; F, 28.2. Found: S, 15.81; Cl, 35.17; F, 27.9.

HCl + $\text{NF}_2\text{CCl}_2\text{S(O)F}$. $\text{NF}_2\text{CCl}_2\text{S(O)F}$ 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 $\text{NF}_2\text{CCl}_2\text{S(O)Cl}$. 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: $\text{FNCCl}_2\text{S(O)Cl}^+$, $\text{NCCl}_2\text{SO}_2\text{Cl}^+$, $\text{NF}_2\text{Cl}_2\text{CS}^+$, NFCCl_2S^+ , $\text{NF}_2\text{CCl}_2^+$, 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

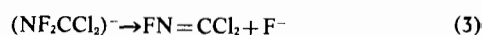
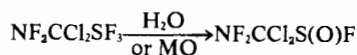
The fluorination and rearrangement of $\text{NF}_2\text{CCl}_2\text{SCl}$ to $\text{CF}_3\text{N}=\text{SF}_2$ in 70% yield³ when KF is present at ambient temperature led us to investigate the products obtained when another fluorinating agent, *i.e.*, AgF_2 , is used under similar conditions. Silver(I) fluoride is found not to react with $\text{NF}_2\text{CCl}_2\text{SCl}$ at 25°.

When the ratio of AgF_2 to $\text{NF}_2\text{CCl}_2\text{SCl}$ is approxi-

mately 1.7 and an oxygen-free environment is maintained, $\text{NF}_2\text{CCl}_2\text{SF}$ 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 $i\text{-C}_3\text{F}_7\text{SF}_6$ which is formed in a pyrolysis reaction at 200° and which behaves similarly in glass. By contrast, $\text{NF}_2\text{CCl}_2\text{SF}$ is very much unlike its closer analogues, $\text{CCl}_{3-n}\text{F}_n\text{SF}$, which isomerize rapidly at 25°. Heating $\text{NF}_2\text{CCl}_2\text{SF}$ at 100° for one hour in Pyrex results in decomposition to SO_2 , $\text{FN}=\text{CCl}_2$, SiF_4 and minor amounts of $\text{NF}_2\text{CCl}_2\text{S(O)F}$. Excess oxygen and $\text{NF}_2\text{CCl}_2\text{SF}$ in Pyrex at 25° gives SO_2 , $\text{FN}=\text{CCl}_2$, SiF_4 and a 25% yield of $\text{NF}_2\text{CCl}_2\text{S(O)F}$. 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 $\text{NF}_2\text{CCl}_2\text{SF}_3$ 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 $\text{NF}_2\text{CCl}_2\text{SF}$ and $\text{NF}_2\text{CCl}_2\text{S(O)F}$, and which are reminiscent of those characteristic of CF_3SF_3 .⁷ Other -SF₃ compounds have also been prepared by the fluorination of sulfur(II)-containing species with AgF_2 .⁸ The presence of $\text{NF}_2\text{CCl}_2\text{S(O)F}$, which is the expected hydrolysis product of $\text{NF}_2\text{CCl}_2\text{SF}_3$ also lends strong support to its preparation in this fluorination reaction.

The quantity of $\text{NF}_2\text{CCl}_2\text{S(O)F}$ obtained varies greatly and is usually low probably due to its subsequent decomposition to $\text{FN}=\text{CCl}_2$ and SOF_2 catalyzed by unreacted AgF_2 as suggested by the following



Therefore, the $\text{NF}_2\text{CCl}_2\text{S(O)F}$ 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 coworkers⁹ suggest that difluoraminoanions are unstable with respect to loss of fluoride ion to form a $\text{FN}=\text{C}$ imine. Since we also observe imine formation ($\text{FN}=\text{CCl}_2$) 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 $\text{NF}_2\text{CCl}_2\text{S(O)F}$ and $\text{NF}_2\text{CCl}_2\text{S(O)Cl}$ at 1268 and 1219 cm^{-1} since no other activity is present in this region. These values compare well with the $\text{CF}_3\text{-}$ analogues, $\text{CF}_3\text{S(O)F}$, 1268 and $\text{CF}_3\text{S(O)Cl}$, 1238 cm^{-1} .⁷

Our attempts to understand the differences in the behavior of the $\text{F}_n\text{Cl}_{3-n}\text{CSCl}$ system and its close ana-

logues, $\text{NF}_2\text{CCl}_2\text{SCl}$ and $\text{CF}_3\text{CCl}_2\text{SCl}$, with fluorinating agents are continuing.

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