with the cold finger. The reactants were heated to 100° for several hours when the mixture darkened. There was some evidence for a small amount of ethane. The addition of BF$_3$ had no effect on these results. All volatile components at $-45°$ were removed. The yellowish liquid did contain a small amount of a PS$_2$F$_2$-containing derivative indicated by the infrared spectrum [bands at 880 (s) and 887 cm^{-1} (m), P—F str; 725 (s) and 705 cm^{-1}, P═S str] and the ^{19}F nmr spectrum [resonance centered at ϕ 11.1 (J = 1195 cps)].

Results and Discussion

Not only is there a difference in the behavior of HPS$_2$F$_2$ toward transition organometal halides and the group IVa alkyl halides, but also there is a marked difference in action of this acid toward the different group IVa organometallic compounds in a related sequence. Stronger conditions are required for the group IVa metallic compounds than for the transition metallic compounds.

However, instead of halogen substitution, which occurs with the transition metal compounds, the alkyl group is displaced when (CH$_3$)$_3$SnCl is used as the substrate. The related germanium and silicon derivatives were unreactive even under the harsher conditions than those used for the tin congener, although there is some evidence for a germanium compound containing the PS$_2$F$_2$ group. On the other hand, when (CH$_3$)$_3$SiH or (CH$_3$)$_3$SiN(C$_2$H$_5$)$_2$ is substituted for the chloride, reaction can be readily achieved below 0°. The hydride requires a catalyst (BF$_3$) while the dialkylamino compound requires no catalyst and (CH$_3$)$_3$SiSP(S)F$_2$ is formed in either case.

The infrared spectra of these compounds exhibit characteristic features. The spectrum of (CH$_3$)$_3$SiSP(S)F$_2$ has bands for which some tentative assignments have been made at 2960 (w) and 2900 (vw) [C—H str], 1416 (w), 1256 (m) [Si(CH$_3$)$_3$], 892 (s) [P—F str], 850 (s) [Si(CH$_3$)$_3$], 765 (wm) [Si(CH$_3$)$_3$], 716 (vs) [P═S str], 625 (wm), 525 (wm), 425 (wm), 385, 365, and *ca.* 340 cm^{-1}, and that of (CH$_3$)$_2$SnClSP(S)F$_2$ has bands at *ca.* 3000 (vw, br) and 2967 (w) [C—H str], 1397 (w) [C—H bend], 884 (s, br) [P—F str], 802 (ms), 707 (vs) [P═S str], 560 (w), 540 (s, sharp), 520 (w), 401 (ms), and 370 cm^{-1}. The ^{19}F nmr spectra show doublet resonance absorptions centered at ϕ 12.2 (J_{P-F_2} = 1200 cps) for (CH$_3$)$_3$SiSP(S)F$_2$ and at ϕ 14.3 (J_{P-F_2} = 1210 cps) for (CH$_3$)$_2$SnClSP(S)F$_2$ while the ^{31}P spectra exhibit triplet resonances centered at -1127 cps (J_{P-F_2} = 1196 cps) and at -1255 cps (J_{P-F_2} = 1210 cps), respectively. The proton spectrum of (CH$_3$)$_3$SiSP(S)F$_2$ has an absorption at τ 9.4, assigned to the methyl group while that of (CH$_3$)$_2$SnClSP(S)F$_2$ absorbs at τ 8.3, also assigned to the methyl group.

The reaction between trimethyltin chloride and oxy acids such as various sulfonic acids[7] and carboxylic acids[8] has been recently investigated. In the former case both the chlorine atom and one methyl group are removed and a bis(sulfonate) is produced. In this procedure the chlorine is reported to be displaced as HCl more facilely than the methyl group as methane. On the other hand, trimethyltin chloride reacts with carboxylic acids to displace only one methyl group as methane,[8] and monocarboxylates are formed. Both these types of oxy acids produce products that are white, crystalline, solid, polymeric substances involving five-[8] and six-coordinated[7] tin.

In this present work, the reaction between the monobasic dithio acid HPS$_2$F$_2$ and trimethyltin chloride causes the displacement of only the methyl group as methane with the formation of a monodifluorodithiophosphate, similar to the examples reported by Wang and Shreeve.[8] Molecular weight measurements of (CH$_3$)$_2$SnClSP(S)F$_2$ as well as of (CH$_3$)$_3$SiSP(S)F$_2$ indicate both are monomeric. Although intermolecular –S–P–S– bridged structures involving bidentate bonding of the S$_2$PF$_2$ group are ruled out, five-coordinated intramolecularly bonded structures cannot be discarded. However, the phosphorous–fluorine coupling constants, *ca.* 1200 cps, are more consistent with a unidentate structure.[1,2,9] In addition, expanded covalencies of the group IVa metals are reported for bonding with only the more electronegative elements such as oxygen. Therefore, structures of the type $\geqslant$M–SP(S)F$_2$ (where M = Si, Ge, Sn) appear to be the more reasonable.

Acknowledgments.—This work was supported in part by the Chemistry Department and in part by the Research Administration of Memphis State University. The authors thank Dr. William H. Graham and Mr. J. A. West of the Rohm and Haas Co., Redstone Research Laboratories, Huntsville, Ala., for the nmr spectra.

---

[7] P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Commun.*, 791 (1969).

[8] C. S. Wang and J. M. Shreeve, *ibid.*, 151 (1970).

[9] The generalization of unidentate or bidentate bonding according to coupling constant data may not be well founded when comparing different sets of compounds.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IDAHO, MOSCOW, IDAHO 83843

Difluoramidosulfuryl Chloride and Dichlorocyanodifluoraminomethane and Its Imine Derivatives[1]

BY L. M. ZABOROWSKI AND JEAN'NE M. SHREEVE*

Received June 30, 1970

Although NF$_2$SO$_2$F is readily prepared by the photolysis of N$_2$F$_4$ and SO$_2$,[2] the sulfuryl chloride analog cannot be obtained using conventional methods for replacing fluorine bonded to sulfur in NF$_2$SO$_2$F by Cl, *e.g.*, with Al$_2$Cl$_6$, R$_3$SiCl, or HCl. However, NF$_2$SO$_2$Cl can be prepared in good yield by photolyzing a mixture of N$_2$F$_4$ and SO$_2$Cl$_2$ at 2537 Å. Although this new compound appears to have reasonable thermal

---

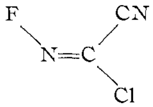
* To whom correspondence should be addressed.

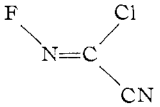
[1] Presented at the Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970.

[2] M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

stability, *e.g.*, more stable than $NF_2S(O)F$[3] but less stable than NF_2SO_2F, it has not proved useful as a synthetic reagent. In every case where typical reactions were attempted, the N–S bond was broken and accompanied in some cases by S–Cl bond cleavage. The usual volatile reaction products are N_2F_4 and SO_2.

The photolytically induced reaction of N_2F_4 with CCl_3CN results in the preparation of the substituted difluoraminonitrile, NF_2CCl_2CN, in yields approaching 10%. The major product is NF_2CCl_3, which is to be expected, since the C–C bond in the totally chlorinated nitrile is easily severed by irradiation with ultraviolet light through quartz to produce $\cdot CCl_3$ radicals which are available to combine with $\cdot NF_2$ radicals. Photolysis of N_2F_4 with other free-radical sources, *e.g.*, polyhaloketones, has been useful in preparing difluoraminopolyhalomethanes, some of which lend themselves to fluorimine formation when treated with mercury. The two imine isomers, FN=C(Cl)-CN, I and II, result in essentially equimolar amounts from dechlorofluorination of NF_2CCl_2CN with mercury.


I


II

Experimental Section

Materials.—Sulfuryl chloride (J. T. Baker) was purified by a trap-to-trap distillation. Trichloroacetonitrile (Columbia Organic Chemicals Co.), 1,3-difluoro-1,1,3,3-tetrachloroacetone (Columbia), chloropentafluoroacetone (Allied Chemical), and tetrafluorohydrazine (Air Products Co.) 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 2-l. Pyrex vessel equipped with a water-cooled quartz probe or in a 120-ml quartz bulb fitted with a Teflon stopcock (Kontes Glass Co.). For gas chromatographic separations, the columns were constructed of 0.25-in. aluminum or copper tubing packed with 20% Kel-F-3 polymer oil, 20% FC-43 (3M Co)., or 10% dimethyl sulfolane (Analabs) 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 457 spectrophotometer by 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 reference. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Two ultraviolet light sources were used: (1) a 450-W lamp (Hanovia L-679A36, Engelhard Hanovia, Inc., Engelhard, N. J.) and (2) a Rayonet "Srinivasan–Griffin" photochemical reactor (Southern N. E. Ultraviolet Co., Middletown, Conn.) fitted with 16 2537-Å reactor lamps.

Preparation and Properties of NF_2SO_2Cl.—SO_2Cl_2 (0.54 g, 0.004 mol) and N_2F_4 (0.21 g, 0.002 mol) were condensed into the 120-ml quartz bulb. After the mixture had warmed to room temperature, it was photolyzed in the "Srinivasan–Griffin" reactor for 4 hr and then passed through traps at −105° (SO_2Cl_2, SO_2, SO_2F_2, NF_2SO_2Cl) and −183° (Cl_2, NF_2SO_2F, SiF_4, N_2F_4). Some N_2 was also noted. Pure NF_2SO_2Cl was obtained by gas chromatography with an 8-ft Kel-F column. An average of a number of runs gives a yield of 62% of purified product based on N_2F_5 consumed.

Difluoramidosulfuryl chloride is a colorless liquid at room temperature which slowly decomposes to Cl_2, SO_2, and N_2F_4 and reacts rapidly with mercury giving SO_2 and N_2F_4 as the volatile products. Because of its thermal instability, vapor pressure data for pure NF_2SO_2Cl were obtainable only up to 323 mm of mercury at 17.5°. An extrapolated boiling point of 38° is obtained from the Clausius–Clapeyron equation $\log P_{\mathrm{mm}} = 8.11 - 1628/T\,°\mathrm{K}$. Vapor pressure data are as follows (T, °K; P, mm): 232.3, 11.9; 241.5, 23.5; 249.2, 37.9; 257, 60.5; 261.2, 76.7; 266.5, 101.9; 273, 140.9; 290.5, 323. The experimental molecular weight was found to be 151.1 (calcd 151.5). NF_2SO_2Cl gives a single broad peak in the ^{19}F nmr at ϕ −55.2. The infrared spectrum (15 mm pressure) is as follows: 1455 (vs), 1214 (vs), 991 (m), 922 (s), 695 (s), 623 (m), 590 (m), 538 (m), 493 (m), 430 cm^{-1} (w). The principal peaks in the mass spectrum correspond to the ions SO_2^{2+}, NF^+, Cl^+, SO^+, NF_2^+, SO_2^+ (100%), and SO_2Cl^+. All chlorine-containing fragments gave the correct isotopic ratios. Basic hydrolysis of NF_2SO_2Cl was used to obtain aqueous solutions for elemental analysis. 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_2SO_2Cl: S, 21.2; Cl, 23.4; F, 25.1. Found: S, 21.0; Cl, 23.5; F, 25.0.

Preparation and Properties of NF_2Cl_2CCN.—Cl_3CCN (2.89 g, 0.020 mol) and N_2F_4 (2.10 g, 0.020 mol) were photolyzed in the 2-l. vessel with the 450-W lamp for 8 hr. NF_2Cl_2CCN and NF_2CCl_3[4] were produced in this reaction and could be obtained in a pure state by gas chromatography with a 25-ft FC-43 column at 0° after trapping the desired fraction at −67°.

Dichlorocyanodifluoraminomethane exists as a stable, colorless liquid at room temperature. The boiling point is 68° from a Clausius–Clapeyron plot described by the equation $\log P_{\mathrm{mm}} = 7.59 - 1612/T\,°\mathrm{K}$. Vapor pressure data are as follows (T, °K; P, mm): 238.1, 10.0; 264.3, 33.8; 273.0, 51.3; 281.3, 79.4; 295.3, 135.8; 304.3, 193.1; 310.3, 267.8; 316.5, 316.1; 320.0, 359.5; 323.0, 399.8; 327.4, 457.7; 329.8, 511.7; 335.5, 574.7; 338, 684.2; 340.8, 764.5. The molar heat of vaporization is 7.38 kcal and the Trouton constant is 21.6. The experimental molecular weight is 160.0 (calcd 160.9). NF_2Cl_2CCN gives a single broad peak in the ^{19}F nmr at ϕ −48.3. The infrared spectrum (11 mm pressure) is as follows: 2262 (m), 1087 (m), 1030 (m), 978 (w), 933 (s), 910–870 (vs, complex), 800 (vw), 724 (w), 648 (m), 490 (w), 455 cm^{-1} (vw). The principal peaks in the mass spectrum correspond to the ions CN^+, N_2^+, CF^+, NF^+, Cl^+, CCN^+, FCN^+, CCl^+, NF_2^+, $(CN)_2^+$ $ClCN^+$, $FNCCN^+$, $ClCCN^+$, CF_2CN^+, $FNCCl^+$, CCl_2^+, CF_2Cl^+, NF_2Cl^+, NF_2CCN^+, $ClFCCN^+$, $FNClCCN^+$, Cl_2CCN^+ (100%), NF_2CClCN^+, and $NF_2CCl_2^+$. All chlorine-containing fragments gave the correct isotopic peak ratios. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany. *Anal.* Calcd for NF_2Cl_2CCN: C, 14.93; N, 17.4; F, 23.6; Cl, 44.06. Found: C, 15.01; N, 17.4; F, 23.9; Cl, 43.83.

Preparation and Properties of I and II.—NF_2Cl_2CCN (0272 g, 1.70 mmol) and excess mercury were stirred at 20–30° in a 125-ml glass vessel fitted with a Teflon stopcock for 3 hr. The volatile products consisted of 0.7 mmol of each isomer of FN=C(Cl)CN plus minor amounts of FN=FCCN and NF_2Cl_2CCN. The products were separated *via* gas chromatography with a 15-ft dimethyl sulfolane column. The assignment of configuration to the two isomers was made by comparison of the ^{19}F nmr spectra with similar compounds.

I and II are colorless, stable liquids at room temperature,

---

[3] R. A. DeMarco, private communication, University of Idaho.

[4] L. M. Zaborowski and J. M. Shreeve, *J. Amer. Chem. Soc.*, **92**, 3665 (1970).

having boiling points in the range 45.5 ± 0.5°. The temperature–pressure dependence for I may be expressed by the equation $\log P_{mm} = 8.17 - 1683/T°K$. Vapor pressure data are as follows (T, °K; P, mm): 257.5, 43.0; 273.0, 101.7; 280.5, 148.0; 287.0, 204.2; 292.3, 255.5; 296.5, 311.7; 300.5, 375.1; 303.5, 423.7; 309.2, 533.7; 311.8, 596.7; 314.8, 656.3; 320.3, 802.8. The molar heat of vaporization is 7.70 kcal and the Trouton constant is 24.2. The experimental molecular weight is 107.7 (calcd 106.5). I shows a single broad peak in the ^{19}F nmr at ϕ −63.4. The infrared spectrum (22 mm pressure) is as follows: 2253 (m), 1560 (m, doublet), 1170 (s, doublet), 1138 (s, doublet), 990–962 (vs, complex), 680 (m, doublet), 541 (w, triplet), 500 (w, doublet), 408 cm^{-1} (w). Peaks were attributed to the following species in the mass spectrum: CN^+, N_2^+, CF^+, Cl^+ (30%), CCN^+, CCl^+, $(CN)_2^+$, $N{=}CCl^+$, $FN{=}CCN^+$ (100%), $ClCCN^+$, $FNCCl^+$, CF_2Cl^+, $N{=}CClCN^+$, $FN{=}CClCN^+$ (93%). The parent, $FN{=}CCN^+$, and Cl^+ were the three major peaks in the spectrum. All chlorine-containing fragments gave the correct isotopic peak ratios. Analysis of chlorine as AgCl and fluorine by specific ion electrode were run. *Anal.* Calcd for I: Cl, 33.3; F, 17.8. Found: Cl, 32.3; F, 18.4.

The temperature–pressure dependence for II can be expressed by the equation $\log P_{mm} = 7.96 - 1621/T°K$. Vapor pressure data are as follows: (T, °K; P, mm): 254.2, 38.3; 272.5, 100.2; 280.0, 149.7; 285, 184.4; 291, 253.7; 296.5, 312.0; 299.3, 352.0; 302.0, 397.0; 308.5, 511.5; 313.8, 625.5; 319.7, 779. The molar heat of vaporization is 7.42 kcal and the Trouton constant is 23.3. The experimental molecular weight is 105.0 (calcd 106.5). II shows a single broad peak in the ^{19}F nmr at ϕ −69.0. The infrared spectrum (20 mm pressure) is as follows: 2249 (m), 1560 (w), 1200 (w), 1135 (s, doublet), 942 (s, triplet), 850 (w), 750 cm^{-1} (w). The peaks in the mass spectrum were assigned to the following species: CN^+, N_2^+, CF^+, Cl^+ (16%), CCN^+, CCl^+, $(CN)_2^+$, $N{=}CCl^+$, $FN{=}CCN^+$ (100%), $ClCCN^+$, $FNCCl^+$, $N{=}CClCN^+$, $FN{=}CClCN^+$ (47%). All isotopic fragments containing chlorine were found in the correct ratio. *Anal.* Calcd for II: Cl, 33.3; F, 17.8. Found: Cl, 33.2; F, 17.0.

N_2F_4 + Perhalogenated Acetones.—N_2F_4 (10 mmol) and $(CFCl_2)_2CO$ (excess) were photolyzed in the 2-l. vessel with a 450-W lamp using a Corex filter for 31 hr. The yield of NF_2CFCl_2 after purification was 30%. N_2F_4 (10 mmol) and $CF_3C(O)CF_2Cl$ (1.83 g, 10.0 mmol) were irradiated in the 2-l. vessel through Vycor for 1 hr. The yield of pure NF_2CF_3[5] was 86 and 71% for NF_2CF_2Cl.[6]

Results and Discussion

Tetrafluorohydrazine was found to react with sulfuryl chloride when irradiated in the gas phase with ultraviolet light of 2537 Å giving difluoramidosulfuryl chloride and chlorine as the main products. The chloride, however, lacks the thermal stability of the fluoride in that it slowly decomposes to N_2F_4, SO_2, and Cl_2 at ambient temperature. As expected, NF_2SO_2Cl reacts rapidly with mercury giving N_2F_4 and SO_2 as the volatile products. With bis(trifluoromethylthio)mercury, N_2F_4 and SO_2 are also obtained along with bis(trifluoromethyl) disulfide, while reaction with bromine fluorosulfate yields N_2F_4, Br_2, and the mixed pyrosulfuryl derivative

$$2NF_2SO_2Cl + (CF_3S)_2Hg \xrightarrow{CH_3CN} N_2F_4 + 2SO_2 + (CF_3S)_2 + HgCl_2$$

$$2NF_2SO_2Cl + 2BrSO_3F \longrightarrow N_2F_4 + Br_2 + 2FSO_2OSO_2Cl$$

It is interesting to compare the products of the latter reaction with those between CF_3SO_2Cl and $BrOSO_2F$[7,8] where the Cl–S bond is severed and a sulfur–oxygen bond results ($CF_3SO_2OSO_2F + BrCl$) while the CF_3–S bond remains essentially intact. With NF_2SO_2Cl, the nitrogen–sulfur bond is fissioned by the positive bromine because of the greater electronegativity of the NF_2 group. NF_2Br, the BrCl analog, is unstable and decomposes to $Br_2 + N_2F_4$.

Dichlorocyanodifluoraminomethane was found to react slowly with mercury at room temperature to form roughly equal amounts of the fluorimino derivatives I and II. The assignment of configuration has been made on the basis of comparison of ^{19}F data with similar known compounds.[9] The chemical shift of the =N—F fluorine was found to move successively downfield when chlorine or cyanide was substituted for the carbon fluorine, which is a result of the increasing paramagnetic contribution of these groups. A comparison of syn and anti isomers indicates that the greatest interaction is between anti groups. Thus, when fluorine is anti to fluorine, the shift is upfield relative to the syn configuration. The stronger interaction of anti groups is also exemplified by larger spin–spin coupling constants than those of the syn isomers. Based on the stronger anti interactions and the greater cyanide deshielding effect than the chlorine deshielding effect, the NF fluorine resonance in the isomer with the CN group anti to the fluorine was assigned to the resonance peak at ϕ −69.0.

Acknowledgments.—Fluorine research at the University of Idaho is sponsored by the National Science Foundation and the Office of Naval Research. The HA-100 nmr spectrometer was funded in part by grants from the National Science Foundation and the Max C. Fleischmann Foundation. We thank Mr. Ron DeMarco and Mr. J. A. Johnson for mass spectra. Special thanks are due Dr. Kent Pullen, Boeing Co., for suggesting the N_2F_4–SO_2Cl_2 reaction.

(5) R. K. Pearson and R. D. Dresner, *J. Amer. Chem. Soc.*, **84**, 4743 (1962).

(6) J. B. Hynes, B. C., Bishop and L. A. Bigelow, *Inorg. Chem.*, **6**, 417 (1967).

(7) R. E. Noftle, *ibid.*, **7**, 2167 (1968).

(8) D. D. DesMarteau, *ibid.*, **7**, 434 (1968).

(9) W. S. Brey, Jr., and J. B. Hynes, *Fluorine Chem. Rev.*, **2**, 111 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

The Photochemical Preparation of Metal–Metal Bonds. II.[1] Some Tin–Manganese and Germanium–Manganese Systems

BY J. K. RUFF[2]

Received July 9, 1970

A large number of manganese carbonyl derivatives in which manganese is bonded to a group IV metal of the general type $R_3MMn(CO)_5$ have been prepared and

(1) Part I: J. K. Ruff, *Inorg. Chem.*, **6**, 1502 (1967).

(2) Alfred P. Sloan Foundation Fellow, 1969–1971.