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Preparation and Defluorosulfurylation of Some N,N-Difluorohydroxylamine O-Fluorosulfate Addition Compounds

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N,N-Difluorohydroxylamine O-fluorosulfate, NF_2OSO_2F, has been added to the unsaturated fluorocarbons tetrafluoroethylene and hexafluoropropylene to form 1-difluoramino-2-(O-fluorosulfato)tetrafluoroethane, $CF_2NF_2CF_2OSO_2F$, in the first instance and the isomeric mixture 1-difluoroamino-2-(O-fluorosulfato)-hexafluoropropane, $CF_3CF(OSO_2F)CF_2NF_2$, and 1-(O-fluorosulfato)-2-difluoroaminohexafluoropropane, $CF_3CF(NF_2)CF_2OSO_2F$, in the other. The addition products underwent defluorosulfurylation to yield perfluoroaminoacetyl fluoride, CF_2NF_2COF, perfluoroaminoacetone, $CF_3COCF_2NF_2$, and perfluoro-α-aminopropionyl fluoride, $CF_3CF(NF_2)COF$, respectively.

Introduction

Since fluorine fluorosulfonate[1] and peroxydisulfuryl difluoride[2] were both found to react with unsaturated fluorocarbons,[3,4] it was of interest to determine whether the recently reported N,N-difluorohydroxylamine O-fluorosulfate[5] would behave in a similar manner. This was found to be the case. A high yield of addition products was formed at elevated temperatures when tetrafluoroethylene and hexafluoropropylene were used as the olefins.

Reaction of these new O-fluorosulfates with alkali metal fluorides resulted in the elimination of sulfuryl fluoride[6] and the formation of an α-difluoroamino ketone when the O-fluorosulfate group is in a nonterminal position and an α-difluoraminoacyl fluoride when the group is in a terminal position.

Experimental

Reagents.—Tetrafluoroethylene was obtained from the pyrolysis of Teflon and purified by vacuum line fractionation. Perfluoropropylene was obtained in 98+% purity from Columbia Organic Chemicals Co., Inc. The NF_2OSO_2F was prepared by the literature method.[5] The alkali metal fluorides were secured from Penn Rare Metals, Inc.

Apparatus.—A standard Pyrex vacuum system was employed for material transfer. The reactor used for the addition of NF_2OSO_2F to the fluoroolefins was a 1-l. Pyrex bulb with an attached capillary mercury manometer. The defluorosulfurylation reactions were performed in a Pyrex bulb containing the dry powdered alkali metal fluoride in large excess.

Measurement of Physical Properties and Analyses.—Infrared spectra were taken in the 2.5–15 μ region with a Perkin-Elmer Infracord using a 10-cm. path length gas cell with NaCl windows (see Table I). Mass spectra were taken using a Consolidated Engineering Corp. Model 21-620 spectrometer with a heated inlet system and an ionizing potential of 100 volts. ^{19}F n.m.r. spectra were obtained with a Varian Model V4310A spectrometer operating at 40 Mc. with CCl_3F used as a standard (see Table II). Molecular weights were taken by vapor density measurements assuming ideal gas behavior. Vapor pressure measurements were obtained by the method of Kellogg and Cady.[7]

For elementary analyses, the total fluorine was found by reducing the compounds with lithium in *n*-propylamine. The nitrogen was determined by Dumas combustion and the carbon by conventional combustion. Identification and determination of per cent composition of components in gaseous mixtures were obtained by *PVT* measurements along with infrared and mass spectral analyses. The mass spectrometer was calibrated using pure samples.

TABLE I

INFRARED SPECTRA OF THE DIFLUORAMINO COMPOUNDS (CM.$^{-1}$)

Compound	Bands
$CF_2NF_2CF_2OSO_2F$	1488 (s), 1351 (m), 1253 (vs), 1219 (ms), 1208 (s), 1192 (ms), 1147 (s), 1081 (s), 978 (s), 934 (s), 873 (ms), 845 (s), 763 (ms)
$CF_3CF(OSO_2F)CF_2NF_2$	1490 (s), 1330 (sh), 1274 (vs), 1189 (s), 1161 (sh), 1139 (ms), 1101 (s), 1015 (m), 962 (m), 943 (ms), 886 (sh), 862 (s), 794 (w), 747 (m), 699 (w)
CF_2NF_2COF	1894 (vs), 1312 (ms), 1259 (s), 1161 (s), 1099 (ms), 982 (m), 941 (ms), 916 (w), 764 (m), 702 (m)
$CF_3CF(NF_2)COF$	1905 (vs), 1315 (ms), 1277 (vs), 1250 (vs), 1164 (s), 1089 (w), 1030 (s), 967 (s), 925 (s), 753 (m), 709 (s)
$CF_3COCF_2NF_2$	1811 (m), 1318 (ms), 1277 (vs), 1250 (vs), 1200 (vs), 1105 (w), 1019 (m), 948 (s), 889 (m), 800 (w), 749 (sh), 730 (ms)

Preparation of $CF_2NF_2CF_2OSO_2F$ (I).—In a typical experiment equimolar quantities of NF_2OSO_2F and C_2F_4 (8.2 mmoles) were placed in the above described reactor and then submerged in an oil bath. The temperature of the reactor was raised slowly to 98–99°, at which point the pressure was observed to decrease. During the next 2.25 hr. the temperature was allowed to increase slowly to 106°. The reaction was quenched by immediate cooling of the reactor to −196°.

The contents of the reactor were fractionated through traps maintained at −126, −145, and −196°. Infrared and mass spectral examination revealed that the fraction collected at −126° was compound I (8.1 mmoles) in high purity and the trap at −196° contained trace quantities of C_2F_4, NF_2OSO_2F, COF_2, and SiF_4. Further rectification of the addition product using a gas chromatograph equipped with a 5-ft. column consisting of Kel-F No. 10 oil, 20% by weight on Chromosorb P, regular, 80/100 mesh, gave a product that was 99+% pure.

Anal. Calcd. for $C_2F_7NO_3S$: N, 5.58; C, 9.56; F, 53.0. Found: N, 5.57; C, 9.66; F, 51.0. The vapor density molecular weight was 253 g./g.m.v. (calcd. 251).

Preparation of the $CF_3CF(OSO_2F)CF_2NF_2$ (II) and $CF_3CF(NF_2)CF_2OSO_2F$ (III) Isomeric Mixture.—Equimolar quantities

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TABLE II

F^{19} N.M.R. SPECTRA

$CF_2NF_2CF_2OSO_2F$

φ	Area ratio	Assignment
−47.6 (triplet)	1.0	SF
−13.9 (broad)	1.8	NF_2
86.3 (quad)	2.0	CF_2 (−OSO_2F)
120.5	2.0	CF_2 (NF_2)

$CF_3CF(NF_2)CF_2OSO_2F$

φ	Area ratio	Assignment
−50.7	1.0	SF
−23.2 (broad)	2.0	NF_2
74.6	3.2	CF_3
78.0	2.0	CF_2
168.8	0.9	CF

$CF_3CF(OSO_2F)CF_2NF_2$

φ	Area ratio	Assignment
−50.7	1.0	SF
−18.0 (broad)	1.9	NF_2
80.8	3.0	CF_3
116.9	1.9	CF_2
142.2	1.1	CF

CF_2NF_2COF

φ	Area ratio	Assignment
−23.8	1.0	O=C—F
−17.8	1.9	NF_2
109.8	2.2	CF_2

$CF_3CF(NF_2)COF$

φ	Area ratio	Assignment
−31.1	1.0	O=C—F
−26.3	1.8	NF_2
75.2	3.2	CF_3
165.7	1.0	CF

$CF_3COCF_2NF_2$[a]

φ	Assignment
−18.2	NF_2
75.0	CF_3
108.9	CF_2

[a] Spectrum too weak to permit area ratio determination.

of C_3F_6 and NF_2OSO_2F (13.0 mmoles each) were placed in the above reactor and the reactor temperature slowly raised. Between 85 and 89° the pressure began to decrease. The reactor was gradually heated to 100° over a 3.25-hr. period. The products were fractionated on the vacuum line using a procedure similar to that above. The combined addition products (12.7 mmoles) were retained in the trap maintained at −80° while only trace quantities of the products CO_2, COF_2, and SiF_3 were found in the trap held at −196°. After further purification by chromatography, using the above column, the mixed isomeric addition compounds were found to contain negligible impurities. Additional attempts to resolve the isomeric mixture by chromatography using a 10-ft. column containing Kel-F on Fluoropack and 5- and 16-ft. columns containing Kel-F on firebrick, either at 0° or at room temperature, were unsuccessful. Therefore, the analysis and molecular weight data were obtained from the mixed isomers.

Anal. Calcd. for the isomers, $C_3F_9NO_3S$: C, 11.96; N, 4.65; F, 56.8. Found: C, 11.96; N, 4.82; F, 56.6. The molecular weight by vapor density was 295 g./g.m.v. (calcd. 301).

Isolation of $CF_3CF(OSO_2F)CF_2NF_2$.—Compound II was isolated in a substantially pure state by treating the isomeric mixture with excess KF (see next section) for 21 hr. at room temperature. The compound was obtained by allowing the reaction products to pass slowly through a trap kept at −80° which retained II.

Anal. Calcd. for $C_3F_9NO_3S$: C, 11.96; N, 4.65. Found: C, 12.05; N, 4.39. Its gas density molecular weight was 299 g./g.m.v. (calcd. 301).

Preparation of CF_2NF_2COF (IV).—Compound I (1.0 mmole) was allowed to stand over several grams of dry KF for 18 hr. at room temperature. After this time *PVT* measurement and mass spectral and infrared analyses revealed 1.9 mmoles of volatile product were present and that it consisted of 1.0 mmole of SO_2F_2 and 0.9 mmole of IV. Negligible quantities of CO_2 and fluorocarbons were detected. The acyl fluoride was purified by prolonged pumping upon the mixture held at −160°. The SO_2F_2 was slowly removed. The chromatographic columns, Kel-F and perfluorotri-*t*-butylamine each on Chromosorb P and Fluorosilicone QF-10995 on Anachrome ABS, were used, but in no case did the acyl fluoride survive chromatography.

Anal. Calcd. for C_2F_5NO: C, 16.1; F, 63.8. Found: C, 15.6; F, 62.7. The average molecular weight by vapor density measurement was 152 g./g.m.v. (calcd. 149).

Preparation of $CF_3CF(NF_2)COF$ (V) and $CF_3COCF_2NF_2$ (VI).—A typical experiment involved the addition of 1.2 mmoles of the mixed C_3F_6–NF_2OSO_2F addition compound to 3 g. of dry KF at −196°. The reactor was warmed to room temperature and after standing 0.5 hr. most of the III was converted to the acyl fluoride, while only a trace of the ketone was formed. The reaction mixture was crudely fractionated by slowly pumping it through traps maintained at −80, −126, and −196°. The unreacted fluorosulfate esters were found in the −80° trap, the crude acyl fluoride and a trace of the ketone in the −126° trap, and the SO_2F_2 in the −196° trap. Further purification was accomplished by passing the acyl fluoride–ketone mixture through a 15-ft. perfluorotri-*t*-butylamine on Chromosorb P column at −45°. Poor resolution was observed with the minor component emerging slightly after the major. The pure acyl fluoride was obtained by allowing part of the acyl fluoride along with the ketone to pass uncollected.

Anal. Calcd. for C_3F_7NO: C, 18.09; N, 7.03. Found: C, 17.83; N, 6.62. The average vapor density molecular weight was found to be 200 g./g.m.v. (calcd. 199).

The ketone VI was prepared by allowing the above unreacted O-fluorosulfate mixture to stand over KF for an additional 20 hr. at room temperature. After this time, III was completely converted to the acyl fluoride; however, some of the II was converted to the ketone. All the products which were volatile at −80° were removed by pumping. The retained II was allowed to stand in contact with KF for several days at room temperature. After this time the reaction was substantially complete. Fractionation through traps maintained at −80, −126, and −196° was adequate for purification. The ketone was found in the −126° trap; however, it contained a trace of the acyl fluoride as shown by the infrared spectrum. A small quantity of CO_2 was again produced.

Mass Spectra.—The following are the mass number, species, and relative abundances for some of the more prominent peaks.

$CF_2NF_2CF_2OSO_2F$: 31, CF^+, 11.1; 47, COF^+, 38.0; 50, CF_2^+, 11.2; 69, CF_3^+, 57.6; 83, FSO_2^+, 100.0; 100, $C_2F_4^+$, 17.0; 119, $C_2F_5^+$, 32.1.

$CF_3CF(OSO_2F)CF_2NF_2$: 31, CF^+, 11.3; 47, COF^+, 11.3; 69, CF_3^+, 71.2; 83, FSO_2^+, 100; 97, $C_2F_3O^+$, 17.8; 169, $C_3F_7^+$, 11.0.

CF_2NF_2COF: 31, CF^+, 18.9; 47, COF^+, 100; 50, CF_2^+, 9.2; 69, CF_3^+, 53.2; 97, $C_2F_3O^+$, 21.8. From the effusion rate of the species corresponding to mass number 47, a molecular weight of 152 was obtained (calcd. 149).

$CF_3CF(NF_2)COF$: 28, CO^+, 7.4; 31, CF^+, 24.6; 47, COF^+, 43.7; 50, CF_2^+, 5.5; 69, CF_3^+, 100; 119, $C_2F_5^+$, 38.1.

$CF_3COCF_2NF_2$: 28, CO^+, 5.8; 31, CF^+, 15.1; 50, CF_2^+, 12.4; 69, CF_3^+, 100; 97, $C_2F_3O^+$, 10.4; 147, $C_2F_5O^+$, 12.4.

Vapor Pressure Measurements.—The vapor pressure of I as a function of temperature was measured. Its boiling point was found to be 52.3°, the Trouton constant 22.83 e.u., and the latent heat of vaporization 7.433 kcal./mole from the Clausius–Clapeyron equation. The equation $\log p = -1625/T + 7.875$ is valid for pressures above 100 mm. No measurements were taken above the boiling point. The vapor pressure data are [given as T (°C.), P (mm.)]: (−11.8, 23.5), (7.1, 113.3), (10.6, 130.4), (12.9, 150.9), (15.3, 168.2), (18.6, 186.1), (19.7, 204.2), (23.9, 229.5), (26.0, 251.3), (31.4, 309.3), (36.2, 394.2), (37.8, 437.8), (39.5, 461.0), (43.5, 513.0), (44.5, 542.4), (46.7, 586.5), (48.3, 637.9).

Results and Discussion

N,N-Difluorohydroxylamine O-fluorosulfate was found to add to tetrafluoroethylene and perfluoropropene in high yield.

$$NF_2OSO_2F + C_2F_4 \longrightarrow \underset{\text{I}}{CF_2NF_2CF_2OSO_2F}$$

$$NF_2OSO_2F + C_2F_6 \longrightarrow \underset{\text{II}}{CF_3CF(OSO_2F)CF_2NF_2} + \underset{\text{III}}{CF_3CF(NF_2)CF_2OSO_2F}$$

The ^{19}F n.m.r. spectrum of the mixture of the two isomers produced in the latter reaction indicated that the ratio of III to II was approximately 2.5:1 by comparing the peak areas due to the different NF_2 and CF_3 groups of each isomer. Unfortunately the isomers could not be separated by either distillation or gas chromatography. No evidence was found for the formation of the symmetrically-substituted products in either of the above reactions.

The reaction of the addition compounds I, II, and III with alkali metal fluorides resulted in defluorosulfurylation.

$$CF_2NF_2CF_2OSO_2F \xrightarrow{KF} \underset{\text{IV}}{CF_2NF_2COF} + SO_2F_2$$

$$CF_3CF(OSO_2F)CF_2NF_2 \xrightarrow{KF} \underset{\text{VI}}{CF_3COCF_2NF_2} + SO_2F_2$$

$$CF_3CF(NF_2)CF_2OSO_2F \xrightarrow{KF} \underset{\text{V}}{CF_3CF(NF_2)COF} + SO_2F_2$$

The reaction of potassium fluoride with the compounds having the fluorosulfate group on a primary carbon (*e.g.*, compounds I and III) was more rapid than when it was on a secondary carbon. This difference in rate was utilized to isolate pure samples of II and was also useful in separating V from VI. The use of either rubidium fluoride or cesium fluoride instead of potassium fluoride in the defluorosulfurylation reaction resulted in an increased rate of reaction. However, many side products were also formed.

The ^{19}F n.m.r. and infrared spectral data on these compounds are presented in Tables I and II. Since the infrared spectra of these materials are complex only a few assignments can be made. The bands attributable to the carbonyl group in compounds IV, V, and VI occur at 1894, 1905, and 1811 cm.$^{-1}$, respectively.[8,9] The asymmetric and symmetric S=O stretching frequencies for the O-fluorosulfate esters are assigned to bands at 1488 and 1253 cm.$^{-1}$ for I, while those for II are at 1490 cm.$^{-1}$ and presumably part of the complex band centering at 1274 cm.$^{-1}$.[10] All the compounds have multiple bands located in the 1330 to 1015 cm.$^{-1}$ region. These are associated with C–F stretching vibrations.[9] The bands observed in the infrared spectra of I, II, IV, V, and VI in the 982 to 925 cm.$^{-1}$ region probably arise from NF vibrations, while the S–F stretching modes are found at 873 and 845 cm.$^{-1}$ and 886 and 862 cm.$^{-1}$ in the spectra of I and II, respectively. The band assigned to the S–O stretching frequency in numerous sulfur oxyfluoride derivatives is found in the 735 to 800 cm.$^{-1}$ region.[11–14] Therefore, it is likely that the bands at 763 and 747 cm.$^{-1}$ in I and II arise from this vibrational mode.

The ^{19}F n.m.r. assignments are presented in Table II. These assignments are based primarily on area ratios and by comparison with previous reported spectra.[6] Certain ^{19}F n.m.r. correlations can be made among the above compounds. The chemical shift of the fluorine bound to the sulfur atom of the fluorosulfate group is relatively invariant (ϕ −47.6 to −50.7). The CF or CF_2 group attached to an NF_2 group appears at higher field than when it is attached to a OSO_2F group. The fluorine of the OSO_2F group in I is split into a triplet by the adjacent CF_2 group. The CF_2 group which is bound to the NF_2 group does not apparently couple with either the adjacent CF_2 group or the NF_2 group. The NF_2, which is broad and unresolved, appears to couple with the CF_2 attached to the OSO_2F group since the band of this CF_2 group appears as four peaks of relative intensities 1:3:3:1 and probably consists of two overlapping triplets.

The chemical and physical characterization of the new compounds prepared in this research are consistent with the structure of the difluoramino O-fluorosulfate esters $CF_2NF_2CF_2OSO_2F$, $CF_3CF(OSO_2F)CF_2NF_2$, and $CF_3CF(NF_2)CF_2OSO_2F$; the α-difluoroaminoacyl fluorides CF_2NF_2COF and $CF_3CF(NF_2)COF$; and the ketone $CF_3COCF_2NF_2$.

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