Sulfonation of Perfluorovinylamines: Synthesis of the First Examples of Nitrogen-Substituted β-Fluorosultones

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β-Fluorosultones, precursors to fluorosulfonyl derivatives, find application in the production of strong sulfonic acids, ion-exchange resins, surface active agents and perfluorinated sulfonate ionomers.[1–6] These compounds are prepared by the well-documented reaction of SO_3 with fluoroolefins,[7,8] fluorovinyl ethers,[9–12] and, more recently, perfluorovinylsulfonyl fluoride.[13] In all these cases the carbon atoms in the four membered β-fluorosultone ring may be bonded to hydrogen, halogens, poly/perfluoroalkyl/alkoxy, or fluorosulfur(VI) substituents, in addition to fluorine.[7,13] The conspicuous absence of a nitrogen substituent in β-fluorosultones, the reactive nature of perfluorovinylamines[14] and the potential that fluoroamine-containing sultones provide for the subsequent preparation of highly stable and unusual fluorinated conducting polymers prompted us to explore the possibility of synthesizing the first nitrogen-substituted β-fluorosultones.

Reactions of perfluorovinylamines with γ-SO_3 can be represented as

$$R_fCF{=}CF_2 + \gamma\text{-}SO_3 \xrightarrow[80\,^\circ C,\ 36\ h\ (II,\ III)]{25\,^\circ C,\ 10\ d\ (I)} R_f\overline{CFCF_2SO_2O}$$

I–III

$$R_f = (CF_3)_2N\ (I),\ \overline{CF_2CF_2CF_2CF_2N}\ (II),\ \overline{CF_2CF_2OCF_2CF_2N}\ (III)$$

Compound **I** is isolated in ~80% yield by carrying out the sulfonation of perfluorovinyldimethylamine at 25 °C for 10 days. Perfluorovinylpyrrolidine and perfluorovinylmorpholine react very slowly under similar conditions but give sultones **II** and **III** in about 65–70% yield when heated at 75–80 °C in a sealed tube for 36 h. Attempts to expedite the formation of **I** by raising the temperature to ~80 °C results in sultone ring opening and the concomitant quantitative formation of the isomerized product $(CF_3)_2NC(O)CF_2SO_2F$ (**IV**). Our attempts to sulfonate $\overline{CF_2CF_2CF_2CF_2CF_2N}CF{=}CF_2$ under different conditions are unsuccessful, and only a trace amount of the isomerized product, $\overline{CF_2CF_2CF_2CF_2CF_2N}C(O)CF_2SO_2F$ is obtained. These conditions are milder than those required for similar reactions with perfluorovinyl ether[12] or fluoroallyl ethers,[15] in keeping with the expected greater reactivity of perfluorovinylamines toward γ-SO_3.

While perfluorovinylamines are found to undergo bidirectional electrophilic addition reactions with ClF, SF_5OCl, $ClOSO_2F$, etc.,[14] the addition of SO_3 is stereospecific to form only a single isomer. The direction of addition of SO_3 to the vinylamine is opposite to that found when SO_3 reacts with fluoroolefins. The product observed results from electrophilic attack of the sulfur atom on the relatively electron rich vinylic difluoromethylene group. A similar effect is observed by Krespan[10] and by Gard[12] in reactions of fluorovinyl ethers with SO_3 and is attributed to a shift of the π-electron cloud toward the difluoromethylene group because of the presence of the nitrogen lone pair of electrons. These results suggest that addition at the difluoromethylene group is to be expected when a substituent bears even a weakly basic lone pair of electrons on the element α to the perfluorovinyl group. This unusual addition is not observed with SF_5-substituted olefins probably because there are no free electrons to influence the electron density of the vinylic system.[2]

The β-fluorosultones **I–III** are colorless, highly moisture sensitive liquids, and with the exception of **I**, are thermally stable to at least 90 °C. The infrared spectra of sultones **I–III** show very strong peaks at ~1452 and ~1260–1224 cm^{-1}, attributable to ν_{as} and ν_sSO_2 stretching frequencies, respectively, in agreement with values reported for other sultones.[2,4,12,16] The ^{19}F NMR spectra show complex AB type multiplets for the CF_2 fluorine atoms of the perfluoropyrrolidine/perfluoromorpholine rings. The nonequivalent CF_2 fluorine atoms of the sultone ring appear in the range δ −93 to −98 ppm as expected.[7,10,12,17] The reverse addition of SO_3 is apparent from the unusually low δ_{CF} ring fluorine resonances observed at δ −85.5 to −92.5 ppm and, the large $^2J_{FF}$ value (155–161 Hz) found for the gem CF_2 fluorine atoms in the sultone ring.[7] In the mass spectrum of **I** (EI) a molecular ion is observed. For **II** and **III**, MH^+ is present in the CI mass spectra.

When either **II** or **III** is reacted with KF, a mixture of products is obtained. The infrared spectra of the liquid obtained in a trap held at −90 °C have bands at 1889 cm^{-1} and in the 1780–1750-cm^{-1} region which are assignable to ν_{CO}. In the ^{19}F NMR spectra resonance bands are found at δ ~44, and ~42.3 ppm arising from fluorine bonded to $-SO_2F$ and at δ ~24 ppm which is in the usual −C(O)F resonance region. No bidirectional addition is occurring, as is reported in the case with chlorotrifluoroeth-

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ylene.[18] Isomerization monitored by ^{19}F NMR leads to the conclusion that there is one product, $FC(O)CF_2SO_2F$,[18,19] common to both mixtures as well as the fluorosulfonyl amides, $CF_2CF_2CF_2CF_2NC(O)CF_2SO_2F$ (**V**) and $CF_2CF_2OCF_2CF_2NC(O)CF_2SO_2F$ (**VI**) that result via ring opening of the sultones **II** and **III**, respectively.

Infrared spectra of **IV–VI** contain very intense bands at 1775, 1774, and 1778 cm^{-1}, respectively, which can be assigned to ν_{CO}. The asymmetric and symmetric SO_2 stretching frequencies for these compounds appear in the regions 1490–1473 and 1270–1240 cm^{-1}, respectively. Stretching bands at 825–800 cm^{-1} are assigned to ν_{SF} and are supported by literature values for other $-SO_2F$-containing compounds.[2,4,12,16] In the ^{19}F NMR spectrum for **IV**, **V**, or **VI**, a triplet resonance at $\sim\delta$ 42 ppm is assigned to the fluorine atom in $-SO_2F$. A group of peaks comprised of doublets of septets centered at δ −101.6 ppm in **IV** or doublets of pentets centered at δ −101.8 in **V** or **VI** arise from coupling of the fluorine atoms of the $-C(O)CF_2$ group with $-SO_2F$ and with CF_3 or CF_2 groups associated with the nitrogen-containing moiety. The $^3J_{FF}$ and $^4J_{FF}$ values for **IV–VI** are 3.7 and 7.4, 3.8 and 13.2, and 4.8 and 12.8 Hz, respectively.

When **II** or **III** is treated with excess cold methanol, methyl (fluorosulfonyl)difluoroacetate forms, which is identified by comparison with reported spectral data.[20] This fact supports the structure of these new sultones where sulfur is bonded to the terminal carbon.[10,12] Also found in the alcoholysis product mixture is CH_3OCH_3 which may result from the interaction of methanol with HF formed *in situ* when the nitrogen containing ring decomposes.

Experimental Section. Sulfur trioxide (Aldrich) is freshly distilled before use. Volatile reactants and products are handled in a Pyrex vacuum line.[14] Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR or Hitachi EPI-G3 spectrometer with a 10-cm glass cell equipped with AgCl windows. ^1H and ^{19}F NMR spectra are obtained on Bruker AC200/300 FT-NMR or a Hitachi R-90F spectrometer by using dry $CDCl_3$ as a solvent. Chemical shifts are referenced to Me_4Si (^1H) or $CFCl_3$ (^{19}F). Coupling constants are obtained from AB type spectra by known procedures.[21,22] Mass spectra are obtained on a Varian VG 7070 HS or a Shimadzu GC/MS Model 7000 mass spectrometer. Elemental analyses are performed by Beller Microanalytisches Laboratorium, Göttingen, Germany. Since the products formed are highly moisture sensitive, all manipulations are performed with the strict exclusion of moisture.

Preparation of Sultones I–III. To freshly distilled sulfur trioxide ($\sim$10 mmol) in a thick-walled Pyrex glass tube ($\sim$200 mL) is transferred the perfluorovinylamine ($\sim$12 mmol) at −196 °C. The tube is then evacuated and sealed. The reaction mixture is allowed to warm to 25 °C and either left at this temperature for 10 days (sultone **I**) or heated at $\sim$80 °C for 36 h (sultones **II** and **III**). The desired sultones are then isolated by trap-to-trap distillation.

Properties of $(CF_3)_2NCFCF_2SO_2O$ (I). This compoud is obtained as a colorless liquid in $\sim$80% yield in a trap held at −78 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1451 s, 1370 vs, 1280 w, 1260 m, 1227 vs, 1142 w, 1074 w, 1028 vw, 1000 sh, 990 m, 872 s, 818 w, 775 m, 743 w, 712 w, 591 m, 513 vw. ^{19}F NMR $[(CF_3^A)_2NCF^BCF_2^{CD}SO_2O]$: δ −54.7 (A, br s), −87 (B, m), −93.6 (C, AB m), −97.8 (D, AB m); J_{CD} = 160.1 Hz. MS EI [*m/e* (species) intensity]: 313 (M^+) 0.9; 297 ($M^+ - O$) 9.1; 233 ($M^+ - SO_3$) 18.2; 214 ($C_4F_8N^+$) 18.2; 183 ($(CF_3)_2NCF^+$) 18.2; 180 ($M^+ - CF_2SO_2F$) 63.6; 164 ($C_3F_6N^+$) 36.4; 133 ($C_2F_5N^+$) 54.5; 114 ($C_2F_4N^+$ or $CF_2SO_2^+$) 100; 97 (CF_2CFO^+) 100; 92 ($COSO_2^-$) 90.9; 83 (SO_2F^+) 18.2; 69 (CF_3^+) 54.8; 64 (SO_2^+) 31.8.

Properties of $CF_2CF_2CF_2CF_2NCFCF_2SO_2O$ (II). This compound is obtained as a colorless liquid in $\sim$68% yield in a trap held at −10 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1452 s, 1433 vw, 1410 m, 1357 s, 1338 s, 1299 ms, 1267 s, 1252 s, 1224 vs, 1187 s, 1139 ms, 1075 m, 1036 ms, 976 vs, 921 m, 873 w, 812 vs, 697 m, 674 w, 641 vw, 609 m, 563 mw, 499 mw, 484 m. ^{19}F NMR $[CF_2^{AB}CF_2^{CD}CF_2^{CD}CF_2^{AB}NCF^ECF_2^{FG}SO_2O]$: δ −85.9 (A, AB m), −92.5 (E, m), −93.0 (F, AB m), −96.6 (B, AB m), −97.9 (G, AB m), −128.9 (C, AB m), −137.3 (D, AB m); J_{AB} = 175 Hz, J_{CD} = 251 Hz, J_{FG} = 155.5 Hz. MS CI [*m/e* (species) intensity]: 376 ($M^+ + 1$) 7.2; 356 ($M^+ - F$) 2.5; 312 ($M^+ + 1 - SO_2$) 5.1; 295 ($M^+ - SO_3$) 2.2; 294 ($C_4F_8NSO_3^+$) 22.6; 292 ($M^+ - SO_2F$) 4.6; 276 ($M^+ - SO_3F$) 2.2; 264 ($C_5F_{10}N^+$) 22.9; 246 ($C_5F_9N^+ + 1$) 9.9; 242 ($C_4F_8NCO^+$) 95.3; 214 ($C_4F_8N^+$) 1.32; 196 ($C_4F_7NH^+$) 65.4; 195 ($C_4F_7N^+$) 17.6; 176 ($C_4F_6N^+$) 61.2; 161 ($C_2F_3SO_3^+$) 8.1; 145 ($C_2F_3SO_2^+$) 24.4; 133 ($C_2F_5N^+$) 4.2; 119 ($C_2F_5^+$) 7.6; 114 ($C_2F_4N^+$ or $CF_2SO_2^+$) 4.5; 111 ($CFSO_3^+$) 5.7; 100 ($C_2F_4^+$) 16.1; 97 ($C_2F_3O^+$) 100, 95 ($CFSO_2^+$) 9.8; 92 ($COSO_2^+$) 30.7; 84 (HSO_2F^+) 24.8; 83 (SO_2F^+) 7.1; 81 (HSO_3^+) 7.8; 79 ($CFSO^+$) 23.9; 78 (CF_2CO^+) 13.7; 69 (CF_3^+) 86.9; 65 (HSO_2^+) 100. Anal. Calcd for $C_6F_{11}NO_3S$: C, 19.2; F, 55.7. Found: C, 17.7; F, 54.0.

Properties of $CF_2CF_2OCF_2CF_2NCFCF_2SO_2O$ (III). This compound is obtained as a colorless liquid in $\sim$71% yield in a trap held at −10 °C. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1452 vs, 1433 w, 1413 w, 1334 s, 1304 vs, 1294 vs, 1263 s, 1228 vs br, 1186 vs, 1157 s, 1093 m, 1036 ms, 972 w, 936 ms, 917 m, 817 ms, 751 vw, 705 m, 637 mw, 604 m, 580 mw, 566 mw, 502 mw, 482 m. ^{19}F NMR $[CF_2^{AB}CF_2^{CD}OCF_2^{CD}CF_2^{AB}NCF^ECF_2^{FG}SO_2O]$: δ −82 (C, AB m), −85.5 (E, m), −86.4 (A, AB m), −87 (D, AB m), −93 (F, AB m), −95.1 (B, AB m), −97.1 (G, AB m); J_{AB} = 198 Hz, J_{CD} = 147 Hz, J_{FG} = 155 Hz. MS CI [*m/e* (species) intensity]: 392 ($M^+ + 1$) 0.1; 372 ($M^+ - F$) 0.4; 328 ($MH^+ - SO_2$) 5.0; 311 ($M^+ - SO_3$) 0.8; 310 ($C_4F_8NSO_4^+$) 11.4; 308 ($M^+ - SO_2F$) 3.6; 292 ($M^+ - SO_3F$) 3.7; 280 ($C_5F_{10}NO^+$) 2.3; 262 ($C_5F_9NO^+$) 4.3; 258 ($M^+ - CF_2SO_2F$) 8.9; 212 ($C_4F_7NOH^+$) 89.8; 192 ($C_4F_6NO^+$) 91.8; 176 ($C_4F_6N^+$) 8.4; 164 ($C_3F_6N^+$) 53.6; 145 ($C_2F_3SO_2^+$) 50.8; 133 ($C_2F_5N^+$) 6.4; 119 ($C_2F_5^+$) 34.8; 114 ($C_2F_4N^+$ or $CF_2SO_2^+$) 24.0; 111 ($CFSO_3^+$) 2.7; 100 ($C_2F_4^+$) 38.5; 99 (SO_3F^+) 8.9; 97 (CF_2CFO^+) 68.3; 95 ($CFSO_2^+$) 22.1; 92 ($COSO_2^+$) 15.9, 83 (SO_2F^+) 18.1; 81 ($C_2F_3^+$) 21.5; 80 (SO_3^+) 3.4; 79 ($CFSO^+$) 20.5; 78 (CF_2CO^+) 92.; 69 (CF_3^+) 53.4; 65 (SO_2H^+) 100. Anal. Calcd for $C_6F_{11}NO_4S$: C, 18.41; F, 53.5. Found: C, 18.34; F, 53.6.

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