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# Synthesis and reactions of the $\beta$-sultone of perfluorovinylsulfonyl fluoride

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## Abstract

Reactions of perfluorovinylsulfonyl fluoride, $CF_2{=}CFSO_2F$ (**1**), with $SO_3$ forms the novel $\beta$-sultone $\overline{O-CF_2-CF(SO_2F)-SO_2}$ (**2**) in good yield. Compound **2** undergoes ring-opening upon heating or reaction with fluoride ion to give $F(O)C-CF(SO_2F)_2$ (**3**). Hydrolysis of **3** and **2** yields the new compounds $CHF(SO_2F)_2$ (**4**) and $HO_3S-CHF-SO_2F$ (**5**), respectively.

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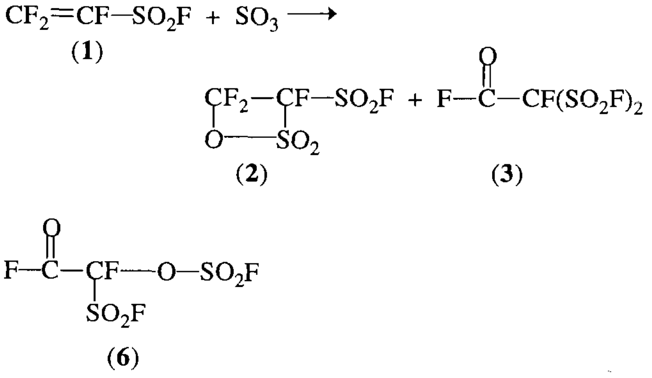
## Introduction

Fluorinated $\beta$-sultones are formed by the reaction of $SO_3$ with a variety of alkenes [1, 2]. These reactive heterocyclic compounds have an interesting chemistry and the sultone of tetrafluoroethylene is the basis of commercial processes for the preparation of perfluorinated sulfonate ionomers [3, 4]. Numerous new reports continue to appear on the chemistry of known and new sultones [5, 6].

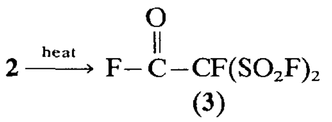
The use of sulfonyl fluorides as precursors to the very acidic bis[(perfluoroalkyl)sulfonyl]imides [6, 7] led us to investigate trifluorovinylsulfonyl fluoride, $CF_2{=}CFSO_2F$ (**1**), as a source of novel sulfonyl fluorides for this purpose. Compound **1** was newly available from the $\beta$-sultone of hexafluoropropene [8] and the $\beta$-sultone of **1** was viewed as a potential new source of bis(sulfonyl fluoride) derivatives. Herein, the synthesis and some reactions of $\overline{OCF_2CF(SO_2F)SO_2}$ (**2**) are reported.

## Results and discussion

The reaction of perfluorovinylsulfonyl fluoride with $SO_3$ requires a high temperature (70–120 °C) and three products are observed. The major product (**2**) is formed by an electrophilic attack by $SO_3$ on the double bond of the olefin in such a way that an oxygen of $SO_3$ is attached to the more positive carbon (i.e. the carbon carrying two fluorine atoms).



The $\beta$-sultone **2** slowly isomerizes to the corresponding acyl fluoride **3** and prolonged heating of **2** increases the amount of the ring-opened isomer **3**.



$$2 \xrightarrow{\text{heat}} F-\overset{\overset{\displaystyle O}{\|}}{C}-CF(SO_2F)_2$$

(**3**)

The isomerization of fluorinated $\beta$-sultones to the corresponding $\alpha$-fluorosulfonylcarbonyl fluorides is well documented [9–11]. At lower temperatures (50–60 °C), ring-opening of the $\beta$-sultone **2** is very slow. At much higher temperatures, a competing reaction occurs and **2** reverts to the starting materials. When a mixture of **2** and **3** was heated at 220 °C, all of the $\beta$-sultone **2** was converted to **1** and $SO_3$ while **3** was recovered unchanged.

The formation of **6**, in very small amounts (~3%) during the preparation of **1**, must arise from an alternative reaction of $SO_3$ with **1**. On the basis of the known chemistry of the reactions of fluoroalkenes with $SO_3$, the pathway for the formation of **1** is not obvious.

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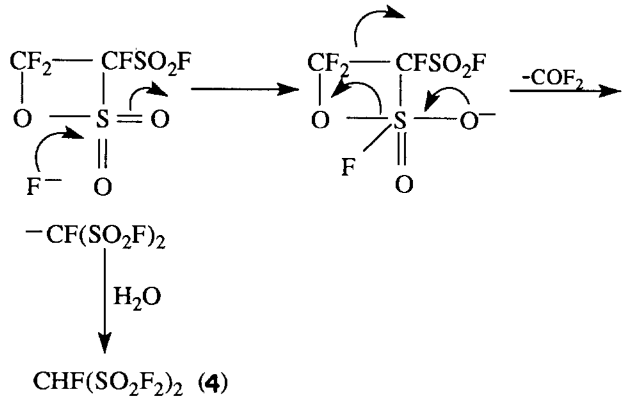


Scheme 1.

Alternative products might have included $CF_2{=}C(SO_2F)OSO_2F$ or $FSO_2CF{=}CFOSO_2F$ [2], but these provide no apparent route to **6**. An alternative structure, i.e. $F(O)CCF(SO_2F)OS(O)F$, can be eliminated based on IR spectroscopy [12].

The IR and NMR spectra strongly support the structure of **6** as indicated with $\nu$(CO) at 1879 $cm^{-1}$ and $\nu$(antisym $SO_2$) at 1498 and 1474 $cm^{-1}$. The $^{19}F$ NMR chemical shifts are quite reasonable for $FC(O)^-$, $SO_2F$ and $OSO_2F$, with the expected coupling constants. Further confirmation of the structure of $F^C(O)C{-}CF^B(SO_2F^D)OSO_2F^A$ was obtained from $^{19}F$ NMR homonuclear decoupling. Upon irradiation of $F^B$ at −138.6 ppm, the other fluorine signals showed reduced multiplicities; $F^C$ and $F^D$ changed from a doublet of doublets to a doublet, and $F^A$ changed from a doublet to a singlet. This established that all the fluorine signals belong to the same molecule and that $F^A$ is more remote from $F^C$ than is $F^D$.

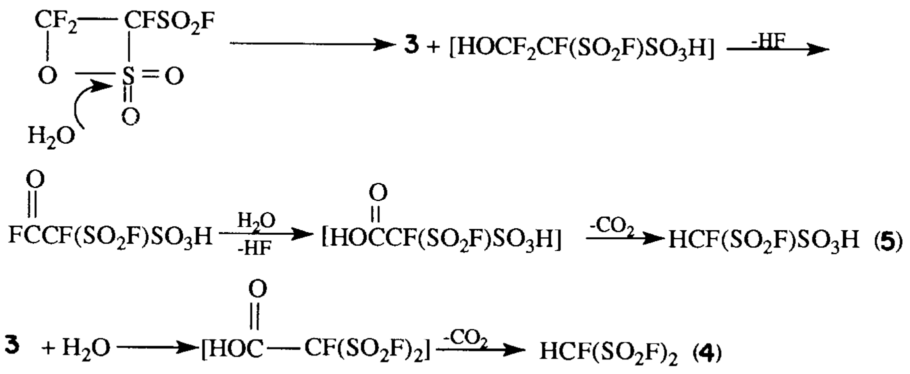
On treatment of **2** with KF, some of the β-sultone is isomerized to **3**, but the major product was $CHF(SO_2F)_2$ (**4**) with $COF_2$ being a by-product. The proton is provided by a small amount of $H_2O$ in the KF. With KF containing 20%–30% $H_2O$, **4** is formed exclusively and $CO_2$ is formed from the hydrolysis of the $COF_2$. Under these conditions, any **3** formed in the reaction is converted to **4** by hydrolysis (see Scheme 2). A reasonable mechanism is shown in Scheme 1. Reaction of **2** with water in the absence of KF, on the other hand, resulted in the formation of **4** in less than 10% yield, with the sulfonic acid $HO_3S{-}CHF{-}SO_2F$ (**5**) being the major product. Scheme 2 shows a reasonable reaction scheme for the formation of **4** and **5** in the absence of KF. Carbon dioxide was isolated and the formation of HF was apparent from attack of the glass by HF.

The sulfonic acid, $H^DO_3S{-}CH^CF{-}SO_2F$, is a colorless non-volatile liquid at 22 °C. The $^1H$ NMR spectrum of **5** in $CD_3CN$ showed a doublet of doublets at $\delta$ 6.4 ppm for $H^C$, and a broadened singlet at $\delta$ 9.0 ppm corresponding to $H^D$. In $D_2O$, the latter signal disappeared due to proton exchange with the $D_2O$. Since **5** is made from the reaction of the β-sultone with excess water, it was not isolated as the anhydrous acid and the position of the resonance for $H^D$ reflects the presence of $H_2O$.

## Experimental

### *General*

A 100 ml two-piece glass reactor containing a Teflon-coated magnetic stirring bar and joined by an Ace–Thred connector fitted with a glass–Teflon valve was used in all reactions. All gases were handled in a glass vacuum system equipped with glass–Teflon valves. Pressures were read from a Wallace and Tiernan differential pressure gauge, series 1500. The amounts of materials were determined by *PVT* measurements or by direct weighing. A Victoreen 4000 series GLC instrument with a thermal conductivity detector was used for preparative gas chromatography. Samples were injected onto a 3 m×3/8 in. Halocarbon (20%)/Chromosorb (60/80) Supelco column using either a 1.0 ml Pressure-Lok Precision gas syringe or a 10 ml Hamilton liquid syringe. The column temperature was kept at 80–100 °C. IR spectra were recorded on a Perkin-Elmer model 1430



Scheme 2.

spectrometer with a model 7500 Data Station. A 10 cm gas cell fitted with KCl windows was used. $^{19}F$ (188.3 MHz) and $^{1}H$ NMR (200.1 MHz) spectra were taken on an IBM NR200AF instrument at ambient temperature. The chemical shifts are reported in $\delta$ (ppm) relative to $CFCl_3$ or TMS with positive shifts at higher frequency than the reference. Mass spectra were obtained on a Hewlett Packard 5985-B spectrometer, at 70 eV for EI and CI ($CH_4$). Samples were introduced by direct gas injection.

*Starting materials*

Although there are three published procedures for the synthesis of $CF_2{=}CFSO_2F$ [13–15], an improved method based on pyrolysis of $CF_3CF(SO_2F)C(O)F$ was employed [8]. Sulfur trioxide, hexafluoropropene and potassium fluoride were obtained from commercial sources.

*Preparation of 1,2,2-trifluoro-2-hydroxy-1-fluorosulfonylethanesulphonic acid sultone (2)*

Into a 100 ml reactor, sulfur trioxide (5.6 mmol) and $CF_2{=}CFSO_2F$ (9.0 mmol) were added by vacuum transfer. The reactor was then heated at 120 °C for 40 h, followed by trap-to-trap vacuum condensation. A small amount of a yellow oil remained in the reactor and did not vacuum transfer at 22 °C. In a −45 °C trap, 4.9 mmol of product was collected. Based on $^{19}F$ NMR analysis, the product consisted of 77% **2**, 20% of 2-fluoro-2,2-bis(fluorosulfonyl)ethanoyl fluoride (**3**) and 2.7% of a compound identified as $F(O)C{-}CF(SO_2F){-}OSO_2F$ (**6**). The products were separated by preparative GLC and the new compounds were characterized as follows:

$O_2\overline{SOCF_2^{A,B}-C}F^C-SO_2F^D$ (**2**): IR (5 Torr) ($cm^{-1}$): 1477 (vs); 1448 (vs); 1314 (s); 1241 (vs); 1218 (vs); 1097 (vs); 836 (w); 816 (s); 785 (s); 735 (w); 660 (s); 617 (s); 581 (w); 524 (s). $^{19}F$ NMR ($CDCl_3$) $\delta$: D 57.2 (d,d,d); C −135.3 (d,d,d); A −80.2 (d,d,d); B −85.5 (d,d,d) ppm; $J_{A-D}=3.4$; $J_{C-D}=4.1$; $J_{B-D}=9.3$; $J_{C-B}=1.8$; $J_{C-A}=7.0$; $J_{A-B}=103.3$ Hz. MS (CI) $m/z$: 245 ($M+1^+$, 56%); 165 ($M-SO_3^+$, 100%). MS (EI) $m/z$: 164 ($M-SO_3^+$, 32%); 81 ($M-S_2O_5F^+$, 19%); 83 ($SO_2F^+$, 16%); 67 ($SOF^+$, 100%); 48 ($SO^+$, 15%).

$F^AC(O)CF^B(SO_2F^C)_2$ (**3**): IR (4 Torr) ($cm^{-1}$): 1878 (s, C=O); 1473 (vs); 1233 (vs); 1135 (m); 1026 (w); 785 (s); 562 (w). $^{19}F$ NMR ($CDCl_3$) $\delta$: A 34.1 (d,t); B −142.2 (d,t); C 55.2 (d,d) ppm; $J_{A-B}=25.9$; $J_{A-C}=6.7$; $J_{B-C}=4.8$ Hz. MS (CI) $m/z$: 245 ($M+1^+$, 100%); 225 $(M-F)^+$; 209 $(M-OF)^+$; 145 $(M-SO_3F)^+$; 83 $(SO_2F)^+$; 67 $(SOF)^+$; 48 $(SO)^+$.

$F^C(O)C-CF^B\ (SO_2F^D)OSO_2F^A$ (**6**): IR (5 Torr) ($cm^{-1}$): 1879 (s, C=O); 1498 (vs); 1474 (vs); 1246 (vs); 1224 (vs); 1139 (s); 1097 (m); 1026 (w); 963 (w); 863 (m); 796 (vs); 710 (vw); 660 (w); 551 (m); 511 (m). $^{19}F$ NMR ($CDCl_3$) $\delta$: A 53.7 (d); B −138.6 (d,t); C 34.7 (d,d); D 56.4 (d,d) ppm; $J_{A-B}=4.8$; $J_{B-D}4.3$; $J_{B-C}=24.8$; $J_{C-D}=6.3$ Hz. MS (CI) $m/z$: 261 $(M+1)^+$.

*Decomposition of 2 at high temperature*

Into a 100 ml reactor, 3.7 mmol of **2** was added by vacuum transfer. The reactor was then heated at 120 °C for 6 d. The volatile products were fractionated through traps held at −24 °C and −196 °C. Based on $^{19}F$ NMR analysis, the −24 °C trap contained **3** and unreacted **2** in a ratio of 1:3.5, respectively. The contents of the −24 °C trap were returned to the reactor and the mixture was heated at 220 °C for 6 d. The product was fractionated by trap-to-trap vacuum condensation at −82, −125 and −196 °C. The −82 °C trap contained 2.7 mmol of $CF_2{=}CFSO_2F$ and $F(O)C{-}CF(SO_2F)_2$ in a ratio of 3.4: 1 ($^{19}F$ NMR spectroscopy), respectively. The −125 °C trap contained 1.4 mmol of $SO_3$ and the −196 °C trap 0.8 mmol of a mixture of $SiF_4$ and $COF_2$.

*Isomerization of 2 by KF*

Into a 100 ml reactor, 2.5 mmol of KF was added. The reactor was evacuated and 3.0 mmol of **2** was added. The suspension was stirred at 25 °C for 6 d. The volatile products were fractionated through traps cooled at −70 °C and −196 °C. The −70 °C trap contained 0.4 g of product which, based on NMR analysis, consisted of $CHF(SO_2F)_2$ and $F(O)C{-}CF(SO_2F)_2$ in a ratio of 3.3:1, respectively. The −196 °C trap contained 1.1 mmol of $COF_2$. About 0.24 g of the starting material was absorbed by the KF. The NMR spectrum of the solid residue did not indicate a salt such as $K^+\ {}^-O{-}CF_2{-}CF(SO_2F)_2$ and was inconclusive. The mixture of $CHF(SO_2F)_2$ and $F(O)C{-}CF(SO_2F)_2$ was separated by preparative GLC and pure fluorobis(fluorosulfonyl)methane, $CHF(SO_2F)_2$ (**4**), was isolated.

$CH^CF^A(SO_2F^B)_2$ (**4**): IR (5 Torr) ($cm^{-1}$): 2960 (w); 1471 (S); 1429 (m); 1244 (s); 1184 (m); 1133 (m); 1056 (m); 871 (m); 828 (s); 795 (m); 638 (w); 562 (s). $^{19}F$ NMR ($CDCl_3$) $\delta$: A −170.3 (d,t); B 54.3 (d,d) ppm. $^{1}H$ NMR ($CDCl_3$) $\delta$: C 6.6 (d,t) ppm; $J_{A-C}=44.3$; $J_{B-C}=3.2$; $J_{A-B}=7.6$ Hz. MS (EI) $m/z$: 197 $(M-H)^+$; 178 $(M-HF)^+$; 131 $(M-SOF)^+$; 67 ($SOF^+$, 100%). MS (CI) $m/z$: 199 ($M+1^+$, 100%); 197 $(M-H)^+$; 179 $(M-F)^+$; 159 $(M-HF_2)^+$.

*Synthesis of fluoro-(fluorosulfonyl)methanesulfonic acid, $HO_3S{-}CHF{-}SO_2F$ (5)*

A 100 ml reactor was charged with 20.0 mmol of distilled water. It was then evacuated at −196 °C and 2.2 mmol of **2** was added. The mixture was stirred at 40 °C for 4 d. A yellow liquid consisting of two phases was obtained. The glass reactor showed extensive etching. The products were fractionated through traps cooled at −30, −90 and −196 °C. Water collected in the −30 °C trap. The −90 °C trap contained 0.5 mmol of $CHF(SO_2F)_2$ and a trace of water. The −196 °C trap contained 1.6 mmol of $CO_2$. A dense liquid (0.26 g) remained in the reactor and could not be vacuum-distilled at 25 °C. The NMR spectrum of this dense liquid indicates that it was $HO_3S-CHF-SO_2F$.

$H^DO_3S-CH^CF^A-SO_2F^B$ (5): IR (neat liquid, on AgCl) ($cm^{-1}$): 3652–3338 (broad, vs); 2117 (broad, w); 1687–1608 (broad, s); 1430 (s); 1253 (s); 1103 (w); 1049 (m); 812–500 (broad, s). $^{19}F$ NMR ($CD_3CN$) $\delta$: A −170.8 (d,d); B 51.9 (d,d) ppm. $^1H$ NMR ($CD_3CN$) $\delta$: C 6.4 (d,d); D 9.0 (s) ppm; $J_{A-C}=44.9$; $J_{A-B}=5.8$; $J_{B-C}=1.2$ Hz. $^{19}F$ NMR ($D_2O$) $\delta$: A −172.6 (d,d); B 50.1 (d,d) ppm. $^1H$ NMR ($D_2O$) $\delta$: C 6.4 (d,d) ppm; $J_{A-C}=44.2$; $J_{A-B}=6.0$; $J_{B-C}=1.2$ Hz.

## Acknowledgment

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