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β-Fluorosultones: synthesis, reactivity, structure and uses

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CONTENTS

A. ABSTRACT

β-Fluorosultones are unique cyclic compounds formed by addition of sulfur trioxide to fluorinated olefins. Their extensive chemistry is due, in large part, to the ease of forming reactive isomeric fluorosulfonyl polyfluorocarbonyl fluorides or polyfluoroalkene fluorosulfates. Their reactions can lead via multipathways to a large number of structurally modified fluorosulfonic acids or precursors such as fluoroalkyl sulfonyl-fluorides, esters, amines, and alkoxides.

B. INTRODUCTION

Sultones are the cyclic esters derived from hydroxyalkane sulfonic acids; they may also be regarded as sulfur analogues of lactones from hydroxycarboxylic acids

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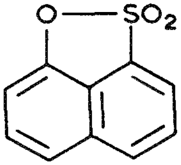
[1,2]. As in the case of lactones, there are α-, β-, γ- and δ-sultones along with a large number of cyclic sulfonates. Among the unsubstituted compounds, the γ- and δ-sultones are the most stable and contain five- and six-membered rings, respectively. Generally, the unsubstituted β-sultones easily decompose and have not yet been isolated, while fluorinated β-sultones are relatively stable [1].

Sulfur trioxide reacts with fluoro-olefins to give stable β-sultones; but with some fluoro-olefins such as tetrafluoroethylene, the final products include a β-sultone, $\overline{CF_2CF_2OS}O_2$, and a β-disultone, $\overline{CF_2CF_2OSO_2OS}O_2$; also mentioned is an eight-membered ring heterocycle, $(\overline{CF_2)_2OSO_2(CF_2)_2OS}O_2$ [3].

Prior to this work, several reviews of fluorinated sultones have been published [1,4]. In the past ten years, a number of important preparative, spectral, and structural works have been reported. The purpose of this review is to update the progress made during this time, and to show that β-fluorosultones are useful in preparing fluorosulfonic acids or their precursors; additional material will be included so as to give the reader a more complete overview of this field.

C. HISTORY OF β-FLUOROSULTONES

The first non-fluorinated β-sultone, 1,8-naphthosultone, was prepared and analyzed in 1887 by Schultz, who credited Menching for its discovery. Later, this compound was studied by Eidmann in 1888, who confirmed the structure and coined the term 'sultone' [2]:



One of the first β-fluorosultones prepared was 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone, $CF_3\overline{CFCF_2OS}O_2$. This β-sultone, which is also named 3-trifluoromethyl-3,4,4-trifluoro-1,2-oxathietane-2,2-dioxide, was made by Jiang in 1957 as a result of direct reaction of sulfur trioxide with hexafluoropropene [5]. Since 1957, over 50 β-fluorosultones have been prepared.

D. PROPERTIES OF β-FLUOROSULTONES

Generally, fluorinated β-sultones are thermally stable, colorless liquids which usually fume in air. They dissolve in saturated hydrocarbons, in fluoro- and chlorohydrocarbons, and in polyhalogeno-olefins. While β-fluorosultones in general are covalent liquids at room temperature, it is surprising to find that the β-fluorosultone $SF_5\overline{CHCF_2OS}O_2$ exists as a solid [6]; only one other β-fluorosultone,

$SF_4(OCH_3)\overline{CHCF_2OSO_2}$, is a solid at room temperature [7]. The crystal structure of $SF_5\overline{CHCF_2OSO_2}$ has been determined [8].

Fluorosultones react with water and many inorganic or organic compounds containing –OH, $-NH_2$, –SCN, and –SH functionality to give derivatives of sulfonic acids or sulfuric acids; some of these derivatives have also been found to have wide chemical applications such as fuel cell electrolytes or additives to fuel cell electrolytes, surfactants, bactericides, or for systems requiring thermally and hydrolytically stable strong acids [1,6,9].

In Table 1, a complete list of known *β*-fluorosultones along with their respective melting or boiling points and IR data is reported.

E. PREPARATION OF *β*-FLUOROSULTONES

The synthesis of *β*-fluorosultones depends on a number of conditions such as temperature, time, impurities, and solvent. The most critical aspect in the synthetic scheme is the generation of monomeric sulfur trioxide, $SO_3(m)$, which reacts with fluoro-olefins:

$$XCF{=}CF_2 + SO_3(m) \rightarrow X\overline{CCF_2OSO_2} \qquad (1)$$

$X = F, CF_3, SF_5, CF_3OCF_2, CF_2{=}CFCF_2, CH_2ClCHClCH_2CF_2$

The generation and handling of monomeric SO_3 can be accomplished in several ways. In one method, trimeric SO_3, $SO_3(t)$, is distilled and the monomeric distillate is then transferred, in a dry box, via a pipet to the reaction vessel. Another method allows for the generation of the $SO_3(m)$ in situ; since the $SO_3(t)$ is unreactive with fluoro-olefins, this method is quite useful and versatile [17,37]. It is important always to start with freshly distilled and pure SO_3. Impurities such as water can lower the overall yield of the sultone or produce side products. In particular, with the impurities B_2O_3, BF_3, or $B(OCH_3)_3$, the following reactions have been observed [32,35,40]:

$$CF_3CF{=}CF_2 + SO_3/BF_3 \rightarrow CF_3\overline{CFCF_2OSO_2} + CF_2{=}CFCF_2OSO_2F \qquad (2)$$

$$(CF_3)_2CFOCF_2CF{=}CF_2 + SO_3/B_2O_3 \rightarrow (CF_3)_2CFOCF_2\overline{CFCF_2OSO_2} + (CF_3)_2CFOCFCF_2OSO_2F \qquad (3)$$

$$C_6F_5CF_2CF{=}CF_2 + SO_3/B_2O_3 \rightarrow C_6F_5\overline{CFCF_2OSO_2} + C_6F_5CF{=}CFCF_2OSO_2F \qquad (4)$$

$$C_3F_7CF_2CF{=}CF_2 + SO_3/B_2O_3 \rightarrow C_3F_7CF_2\overline{CFCF_2OSO_2} + C_3F_7CF{=}CFCF_2OSO_2F \qquad (5)$$

A method of preparing the *β*-fluorosultone $CF_3\overline{CFC(CF_3)_2OSO_2}$, involves the

TABLE 1

β-Fluorosultones

Sultone	BP/IR (cm^{-1})^{a}	Ref.
$\overline{CF_2CF_2OS}O_2$	42°C SO_2 (asym, 1451; sym, 1235) CF (1030–1090)	10–14
$\overline{CFBrCF_2OS}O_2$	–	15
$\overline{CFClCF_2OS}O_2$^{b}	mixture	
$\overline{CF_2CFClOS}O_2$^{b}	73–77°C	5,10,11,16
$\overline{CFClCFClOS}O_2$	110–113°C	11
$\overline{CCl_2CF_2OS}O_2$	110–112°C	11
$SF_5\overline{CFCF_2OS}O_2$	88°C SO_2 (asym, 1448; sym, 1214) CF (1020–1096) SF (stret, 854–896; def, 596)	17,18
$SF_5\overline{CHCF_2OS}O_2$	108–111°C/600 mm; m.p. 47–48°C SO_2 (asym, 1419; sym, 1203) CF (1078–1106) SF (stret, 819–878; def, 612)	18,6
$SF_5\overline{CClCF_2OS}O_2$	–	7
$SF_4{=}\overline{CCF_2OS}O_2$	– SO_2 (asym, 1415; sym, 1192–1235) SF (stretching, 857–874)	19
$ClSF_4\overline{CHCF_2OS}O_2$	– SO_2 (asym, 1430; sym, 1214); SF (stretching, 814–853)	19

$SF_4(OCH)_3)\overline{CHCF_2OS}O_2$	m.p. 21°C	7
$SF_4(OCH(CH_3)_2)\overline{CHCF_2OS}O_2{}^c$	–	7
$\overline{CHFCF_2OS}O_2$	97°C SO_2 (asym, 1455; sym, 1239) CF (1050–1129); CH (2890)	10,11,13,14
$FSO_2\overline{CHCF_2OS}O_2$	49–51°C/15 mm	20
$\overline{CFICF_2OS}O_2$	–	15
$CF_3\overline{CFCF_2OS}O_2$	46.5°C SO_2 (asym, 1455; sym, 1237) CF (1005–1340)	10–14
$CF_3\overline{CHCF_2OS}O_2$	92°C	21
$(CF_3)_2\overline{CCF_2OS}O_2$	63°C	22
$CH_3O\overline{CFCClFSO_2O}$	39–40°C/3 mm	23
$C_2F_5\overline{CFCF_2OS}O_2$	66°C	24
$CF_2ClCF_2\overline{CFCF_2OS}O_2$	103°C	24
$CFCl_2CF_2\overline{CFCF_2OS}O_2$	129–131.5°C	5,16
$CF_2HCF_2\overline{CFCF_2OS}O_2$	90°C	24
$(CF_3)_2\overline{CCF(CF_3)SO_2O}$	–	25
$C_2H_5O\overline{C(CF_3)CF_2SO_2O}$	–	26
$C_2H_5O\overline{CFCFClSO_2O}$	41–42°C/3 mm	23
$CF_3CCl(\overline{O)CCl(S}O_2)CF_3$	132–133.8°C	5,16
$CF_3OCF_2\overline{CFCF_2OS}O_2$	69–72°C SO_2 (asym, 1446; sym, 1249)	27

TABLE 1 (*continued*)

Sultone	BP/IR (cm^{-1})^a	Ref.
$CF_2{=}CF\overline{CFCF_2SO_2O}$	22.5–23°C/30 mm	28
$CF_2{=}CFCF_2\overline{CFCF_2OSO_2}$	100–102°C SO_2 (asym, 1450); $CF_2{=}CF$ (1795)	29
$C_3F_7O\overline{CFCF_2SO_2O}$	66°C/180 mm	26
$C_4F_9O\overline{CFCF_2SO_2O}$	85–90°C/197 mm SO_2 (asym, 1449; sym, 1221)	30
$CF_2ClCFClCF_2\overline{CFCF_2OSO_2}$	55°C/25 mm SO_2 (asym, 1440)	5,31
$(CF_3)_2CFOCF(\overline{O)CF(SO_2})CF_3$	105–107°C	32
$(CF_3)_2CFOCF_2\overline{CFCF_2OSO_2}$	107–109°C SO_2 (asym, 1445)	32,33
$CF_3OCF_2CF_2OCF_2\overline{CFCF_2OSO_2}$	88°C/336 mm SO_2 (asym, 1449; sym, 1225)	27
$(CF_3)_2CFOCF(\overline{O)CF(SO_2})CF_2OSO_2F$	51°C/5 mm SO_2 (asym, 1445); CF,CO,SO_2 (1100–1300) OSO_2F (1490)	33
$CH_2ClCHClCH_2\overline{CFCF_2OSO_2}$	65–68°C/10 mm SO_2 (asym, 1413; sym, 1203) CF (1059–1300)	34
$C_4F_9\overline{CFCF_2OSO_2}$	114°C	24,35
$C_4H_9\overline{CFCF_2OSO_2}$	63–65°C/20 mm	11
$C_5F_{11}\overline{CFCF_2OSO_2}$	134–136.5°C SO_2 (asym, 1450)	36

$CF_2Cl(CF_2CFCl)_2CFCF_2OSO_2$	56–58°C/0.22 mm	5,16
$H(CF_2)_6CFCF_2OSO_2$	76°C/22 mm	11
$CF_2Cl(CF_2CFCl)_3CFCF_2OSO_2$	81–82°C/0.08 mm	5,16
$CF_2{=}CF(CF_2)_2CFCF_2OSO_2$	115°C (est.), 79 ± 1°C/226 mm SO_2 (asym, 1441; syn, 1216) $CF_2{=}CF$ (1785)	31,37
$CF_2{=}CF(CF_2)_4CFCF_2OSO_2$	62–63°C/15 mm	38
$[CF_2(O)CF(SO_2)CF_2]_2$	69 ± 1°C/15 mm SO_2 (asym, 1441; sym, 1216)	37
$[CF_2(O)CF(SO_2)(CF_2)_2]_2$	91–92°C/15 mm	38
$C_6F_5CF_2CFCF_2OSO_2$	–	35
$CF_2Cl(CF_2CFCl)_4CFCF_2OSO_2$	115–116°C/0.4 mm	5,16
$c\text{-}C_{10}F_8OSO_2$[d]	–	39

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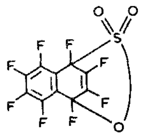
[a] The assignment for symmetric stretching band is complicated in some cases by the appearance of strong carbon–fluorine absorption bands in the 1110–1300 cm^{-1} region.

[b] There is some doubt as to whether these isomers are formed [1,4].

[c] This sultone is stable in solution [7].

[d] Since the chemical composition is not verified, this material may be a pyrosulfate [4].



reaction of CF_3CFHSO_2F with $Me_3N{-}SiF_4$ in the presence of $(CF_3)_2C{=}O$. Extension of this procedure has supposedly yielded a series of β-fluorosultones [25].

It has been reported that reaction of hexafluoroisobutenylidene sulfate with fluoro-olefins produces the corresponding sultones [41].

The chemical nature of the starting olefin can lead to isomeric or reverse addition-type products; with $R_fOCF{=}CF_2$ ($R_f = C_3F_7$, and C_4F_9) and $ClCF{=}CF_2$-type olefins, the following products have been reported [11,26,30]:

$$R_fOCF{=}CF_2 + SO_3 \rightarrow R_fO\overline{CFCF_2SO_2O} \tag{6}$$

$$2ClCF{=}CF_2 + SO_3 \rightarrow Cl\overline{CFCF_2OSO_2} + Cl\overline{CFCF_2SO_2O} \tag{7}$$

Substitution of hydrogen on the carbon which is part of the double bond, can also affect the yield and product distribution. A decreasing tendency toward formation of β-fluorosultones was found for $CF_2{=}CF_2$, $CFH{=}CF_2$, and $CH_2{=}CF_2$; byproducts were thought to be the corresponding cyclic sulfonate-sulfate anhydrides. In the case of $CF_2{=}CFH$, the resulting byproduct is $\overline{CF_2CHFSO_2OSO_2O}$ [11]. It is possible to substitute hydrogen in positions other than at the olefinic carbon and obtain the desired β-fluorosultones [34]:

$$ClCH_2ClCHCH_2CF{=}CF_2 + SO_3 \rightarrow ClCH_2ClCHCH_2\overline{CFCF_2OSO_2} \tag{8}$$

However, the presence of hydrogen in the chain requires lower temperatures in order to prevent attack by $SO_3(m)$ on C–H bonds.

In addition to fluoroalkenes, mono/bis β-fluorosultones can also be prepared from fluorodienes:

$$CF_2{=}CFCF{=}CF_2 + SO_3 \rightarrow CF_2{=}CF\overline{CFCF_2SO_2O} \tag{9}$$

$$CF_2{=}CF(CF_2)nCF{=}CF_2 + \begin{cases} SO_3 \rightarrow CF_2{=}CF(CF_2)_n\overline{CFCF_2OSO_2} & (10) \\ SO_3 \rightarrow [CF_2(\overline{O)CF(SO_2})(CF_2)_n]_2 & (11) \end{cases}$$

Only a few bis-fluorosultones are known [28,37,38].

More recently, the synthesis of the exocyclic β-fluorosultone $F_4S{=}\overline{CCF_2OSO_2}$ has opened a new pathway for preparing SF_5 containing β-fluorosultones [7,19]:

$$F_4S{=}\overline{CCF_2OSO_2} + XY \rightarrow YSF_4\overline{CXCF_2OSO_2} \tag{12}$$

$X = H$ $Y = F, Cl, CH_3O, (CH_3)_2CHO$

$X = Cl$ $Y = F$

In addition to liquid SO_2 [29], other solvents used with SO_3 in forming β-fluorosultones have been 1,1,2-trichloro-trifluoroethane (Freon 113) [16] and dimethyl sulfate [10].

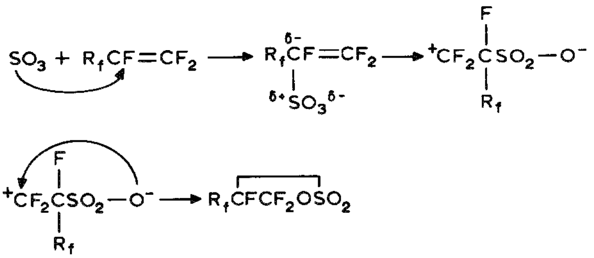
F. MECHANISMS FOR THE FORMATION OF THE β-FLUOROSULTONES

There are three different proposed mechanisms for the reaction of sulfur trioxide with fluoro-olefins.

(i) Electrophilic mechanism

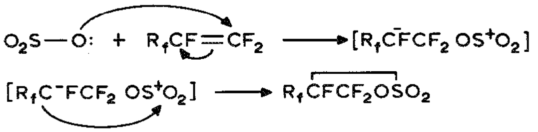
The reaction of sulfur trioxide and fluoro-olefins is proposed as an electrophilic reaction because of the electrophilic character of sulfur trioxide which easily adds to amines, ethers, alcohols, alkyl halides, hydrogen halides, water, and finally fluoro-olefins [10].

Sulfur trioxide reacts with fluoro-olefins through an unshared electron pair of the sulfur heteroatom and the π component of the multiple bond. The resulting intermediate π complex isomerizes into a dipole intermediate, where the sulfur atom is bonded covalently to the carbon atom having enhanced electron density. Finally, through cyclization of the dipole structure, the fluorinated β-sultones are formed [10,42]:



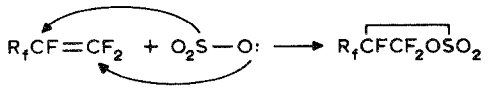
(ii) Nucleophilic mechanism

In this proposed scheme, a lone pair of electrons on an oxygen of sulfur trioxide attacks the carbon of the CF_2 group and forms an intermediate in which the sulfur is positively charged and the adjacent carbon of the CF group is negatively charged. In the final step, the carbon of the CF group and the sulfur undergo ring closure forming the sultone ring [11,17]:



(iii) Concerted mechanism

This scheme is the final possible mechanism for the formation of the mono-β-fluorosultones in which the sulfur and the oxygen of sulfur trioxide attack the carbon of the CF and CF_2 groups simultaneously, and form a β-sultone [43]:



G. REACTIONS OF β-FLUOROSULTONES

(i) Rearrangement

In the presence of various nucleophiles (metal fluorides, amines, alcohols), the fluorosultones undergo rearrangement to their isomeric form, α-fluorosulfonyl polyfluoro carbonyl fluorides:

$$ZCXCF_2OSO_2 \xrightarrow{Et_3N \text{ or } MF} ZCX(SO_2F)C(O)F \tag{13}$$

Z = SF_5, X = F [17]; and SF_5, H [6]

Z = Cl, X = Cl; F, F; F, H; and CF_3, F [11]

Z = FSO_2, X = H [20]; CF_2=$CF(CF_2)_n$ (where $n = 2$ or 4), F [37,38]

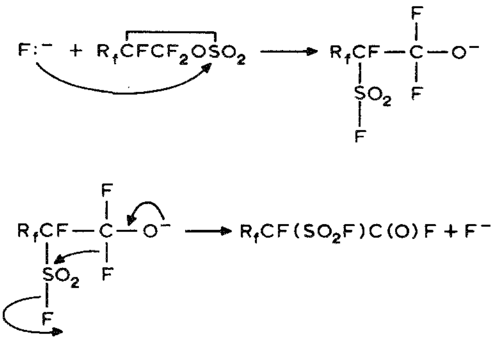
Z = CF_3OCF_2, X = F; $CF_3OC_2F_4OCF_2$, F [27]; $C_3H_5Cl_2$, F [34]

M = Na, K, and Ca

In the case of a sultone derived from fluorovinyl ether, the rearrangement reaction yields an ester [30]:

$$C_4F_9OCFCF_2SO_2O \xrightarrow{NaF} C_4F_9OC(O)CF_2SO_2F \tag{14}$$

A suggested mechanism for the rearrangement of a number of different β-fluorosultones is [1,11,17]:



Bis-fluorosultones also undergo similar rearrangement [37,38]:

$$[\mathrm{CF_2(\overline{O)CF(S}O_2)(CF_2)_2]_2} \xrightarrow{\mathrm{CaF_2}} [\mathrm{FC(O)CF(SO_2F)(CF_2)_2]_2} \quad (15)$$

$$[\mathrm{CF_2(\overline{O)CF(S}O_2)CF_2]_2} \xrightarrow{\mathrm{NaF}} [\mathrm{FC(O)CF(SO_2F)CF_2]_2} \quad (16)$$

Polyfluorochlorosultones can lead by rearrangement to the corresponding sulfonyl chloride product [11]:

$$\overline{\mathrm{CFClCF_2OS}}\mathrm{O_2} \xrightarrow{\mathrm{Et_3N}} \mathrm{CFCl(SO_2F)C(O)F} \quad (17)$$

$$\overline{\mathrm{CFClCFClOS}}\mathrm{O_2} \xrightarrow{\mathrm{Et_3N}} \mathrm{CFCl(SO_2Cl)C(O)F} \quad (18)$$

With an SF_5-sultone, not only rearrangement but dehydrofluorination was found [44]:

$$\mathrm{SF_5\overline{CHCF_2OS}O_2} \xrightarrow{\mathrm{MF}} \mathrm{SF_5CH(SO_2F)C(O)F + SF_5C(SO_2F){=}C{=}O} \quad (19)$$

A second kind of isomerization has also been reported for $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$ and occurs on storage at room temperature [1]:

$$\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2} \rightarrow \mathrm{F_2C{=}CFOSO_2F} \quad (20)$$

In one report, it was found that $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$ purified by gas chromatography upon standing at $-78°C$ for several days formed a chain-like polymer [1]; this material, however, is not stable.

(ii) Hydrolysis reactions

In general, β-fluorosultones with water undergo catalytic rearrangement followed by hydrolysis; for example, in the following two β-fluorosultones, the end products are carboxylic acids and HF [11,10,34]:

$$\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{FSO_2CF_2C(O)OH + HF} \quad (21)$$

$$\mathrm{CH_2ClCHClCH_2\overline{CFCF_2OS}O_2 + H_2O} \rightarrow \mathrm{CH_2ClCHClCH_2CF(SO_2F)C(O)OH + HF} \quad (22)$$

For all other β-fluorosultones, the resulting carboxylic acid is unstable and decomposes:

$$\mathrm{Z\overline{CXCF_2OS}O_2 + H_2O \rightarrow ZCXHSO_2F + CO_2 + HF} \quad (23)$$

$Z = SF_5$, $X = F$ [17]; and SF_5, H [6]

$Z = CF_3$, $X = F$ [11]; CF_3, H [21]; $CF_2ClCFClCF_2$ and

$CF_2{=}CF(CF_2)_2$, F [31]; $CF_3OC_2F_4OCF_2$, F; and CF_3OCF_2, F [27]

$Z = C_2F_4H$, C_2F_4Cl, C_2F_5, C_4F_9; $X = F$ [24]

$Z = CF_2{=}CF(CF_2)_4$, $X = F$ [38]; $CF_2{=}CF(CF_2)_2$, F [37]; and
$CF_2{=}CFCF_2$, F [29]

With bis-fluorosultones, hydrolysis also leads to decarboxylation [37,38]:

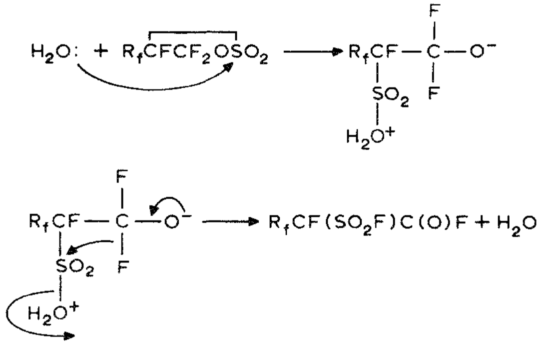
$$[CF_2(\overline{O)CF(S}O_2)(CF_2)_2]_2 + \text{xs. } H_2O \rightarrow [FSO_2CFH(CF_2)_2]_2 + 2CO_2 + 2HF \tag{24}$$

$$[CF_2(\overline{O)CF(S}O_2)CF_2]_2 + \text{xs. } H_2O \rightarrow [FSO_2CFHCF_2]_2 + 2CO_2 + 2HF \tag{25}$$

In the case of the sultone derived from fluorovinyl ether, the hydrolysis reaction yields an ester [32]:

$$(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_3 \xrightarrow{H_2O} (CF_3)_2CFOC(O)CF(CF_3)SO_2F \tag{26}$$

In general, the mechanism for the hydrolysis process is [1,6,27,37,45]:



$$R_fCF(SO_2F)C(O)F + H_2O \longrightarrow [R_fCF(SO_2F)C(O)OH] + HF$$
$$[R_fCF(SO_2F)C(O)OH] + H_2O \longrightarrow [R_fCF(SO_2F)C(O)O^-] + H_3O^+$$
$$[R_fCF(SO_2F)C(O)O^-] \longrightarrow [R_f\bar{C}F(SO_2F)] + CO_2$$
$$[R_f\bar{C}F(SO_2F)] + H_3O^+ \longrightarrow R_fCFHSO_2F + H_2O$$

The pathway for hydrolysis is affected by the acidity/basicity of the solution. The hydrolysis products of the fluoro-β-sultones, such as $X\overline{CFCF_2OSO_2}$ (where X = F and CF_3) in basic and acidic media, yields the following derivatives [1]:

$$\overline{CF_2CF_2OSO_2} + \begin{cases} OH^-(aq) \rightarrow HOC(O)CF_2SO_3H + 2HF & (27) \\ H^+(aq) \rightarrow HOSO_2F + OHC\text{–}C(O)OH + 3HF & (28) \end{cases}$$

$$CF_3\overline{CFCF_2OS}O_2 + \begin{cases} OH^-(aq) \rightarrow CF_3CHFSO_3H + 2HF + CO_2 & (29) \\ H^+(aq) \rightarrow HOSO_2F + CF_3CHFC(O)OH + HF & (30) \end{cases}$$

(iii) Reaction with alcohols/alkoxides

A convenient synthesis of fluoroesters involves using β-fluorosultones with alcohols. The pathway for these reactions first involves rearrangement of the β-fluorosultones followed by reaction with the alcohol in the presence of a base:

$$Z\overline{CXCF_2OS}O_2 + ROH + MF \rightarrow ZCX(SO_2F)C(O)OR + MHF_2 \qquad (31)$$

$Z = SF_5$, $X = H$

$R = CF_3CH_2$, $(CF_3)_2CH$ [6], $CH_2{=}CHCH_2$ [46], $(CH_3)_2CH$ [44]

$Z = SF_5$, $X = F$

$R = CF_3CH_2$, $(CF_3)_2CH$ [6], $CH_2{=}CHCH_2$ [46]

$Z = CF_3$ $X = F$

$R = C_2H_5$, $CH_2{=}CHCH_2$, CF_3CH_2, $(CF_3)_2CH$, C_6F_5 [47],
$C_4H_9CH(C_2H_5)CH_2$ [11], CH_3, C_2H_5 (where $X = H$) [21]

$M = Na$, K, or Li

$Z = F$ $X = F$

$R = C_3H_7$, C_6H_5, C_8H_{17}, $H(CF_2)_4CH_2$ [11], CF_3CH_2, $(CF_3)_3C$,
C_6F_5 [47], CF_3CH_2, $CF_3(CH_3)CH$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$,
$(CF_3)_2CH$, $(CF_3)_2C(CH_3)$, $C_3F_7CH_2$, $CH_2(CF_2)_3CH_2$,
$C_7F_{15}CH_2$ [48], $CH_2{=}CHCH_2$ [46]

$M = Na$, K, or Li

$$Z\overline{CXCF_2OS}O_2 + ROH + NaF \rightarrow ZCX(SO_2F)C(O)OR + NaHF_2 \qquad (32)$$

$Z = CF_3OC_2F_4OCF_2$, $X = F$; CF_3OCF_2, F [27]

$Z = CF_2{=}CF(CF_2)_2$, $X = F$ [37]

$R = CH_2{=}CHCH_2$

In a series of reactions with $CF_2{=}CF(CF_2)_2\overline{CFCF_2OS}O_2$ and $CH_2{=}CHCH_2OH$, the polyester $(CF_2{=}CF(CF_2)_2CF(SO_2F)C(O)OCH_2CHCH_2\text{-})_n$ was produced. For a bis β-fluorosultone, the corresponding bis ester is produced [37]:

$$[CF_2(\overline{O)CF(S}O_2)CF_2]_2 + 2CH_2{=}CHCH_2OH + 2NaF \rightarrow$$
$$[CF_2CF(SO_2F)C(O)OCH_2CH{=}CH_2]_2 + 2NaHF_2 \tag{33}$$

Polymerization of the diester gave $[(\text{–}CH_2CHCH_2OC(O)CF(SO_2F)CF_2)_2]_n$, a solid polymer that is stable above 250°C [37].

When polyhydroxy alcohols were employed for the reaction with β-fluorosultones, the following polyesters were reported [6,11,47]:

$$2SF_5\overline{CFCF_2OS}O_2 + [HOCH_2CF_2]_2CF_2 + 2NaF \rightarrow$$
$$[SF_5CF(SO_2F)C(O)OCH_2CF_2]_2CF_2 + 2NaHF_2 \tag{34}$$

$$2Z\overline{CFCF_2OS}O_2 + [HOCH_2]_2 + 2NaF \rightarrow$$
$$[ZCF(SO_2F)C(O)OCH_2]_2 + 2NaHF_2 \tag{35}$$

$Z = F$, $Z = CF_3$

$$ZCH_n(CH_2OH)_{3-n} + (3-n)\overline{CF_2CF_2OS}O_2 \rightarrow$$
$$ZCH_n(CH_2OC(O)CF_2SO_2F)_{3-n} \tag{36}$$

$Z = CH_3$, NO_2, $OC(O)CF_2SO_2F$, $CH_2OC(O)CF_2SO_2F$

$n = 0, 0, 2, 0$ [48]

With polyvinyl alcohol, the corresponding polyesters were formed [46]:

$$Z\overline{CFCF_2OS}O_2 + [CH_2CHOH]_n + NaF \rightarrow$$
$$[ZCF(SO_2F)C(O)OCHCH_2\text{–}]_n + NaHF_2 \tag{37}$$

$Z = F$ and CF_3; $n \approx 318$, soluble in acetone; decomposes at 120°C, 170°C.

The β-fluorosultones formed from the fluorovinyl ethers react with excess cold methanol to produce fluoroesters. A mechanism explaining this result has been formulated [26,30]:

$$ZOCF(\overline{O)CF_2(S}O_2) + \text{xs. } CH_3OH \rightarrow CH_3OC(O)CF_2SO_2F + Z'C(O)OCH_3 \tag{38}$$

$Z = C_3F_7$, C_4F_9; $Z' = C_2F_5$, C_3F_7

For the exocyclic sultone $F_4S{=}\overline{CCF_2OS}O_2$, reaction with different alcohols has been studied. With CH_3OH, a new β-fluorosultone was isolated but attempts to isolate the β-fluorosultone, $SF_4(OCH(CH_3)_2)\overline{CHCF_2OS}O_2$, in eqn. (40) failed; NMR studies confirmed its existence [7]:

$$SF_4{=}\overline{CCF_2OS}O_2 + CH_3OH \rightarrow SF_4(OCH_3)\overline{CHCF_2OS}O_2 \tag{39}$$

$$SF_4{=}\overline{CCF_2OS}O_2 + (CH_3)_2CHOH \rightarrow SF_5CH(SO_2F)C(O)OCH(CH_3)_2$$
$$+ SF_4(OCH(CH_3)_2)\overline{CHCF_2OS}O_2 \tag{40}$$

With $(CH_3)_3COH$, only the resulting ester was found:

$$SF_4{=}\overline{CCF_2OS}O_2+(CH_3)_3COH\rightarrow SF_5CH(SO_2F)C(O)OC(CH_3)_3 \tag{41}$$

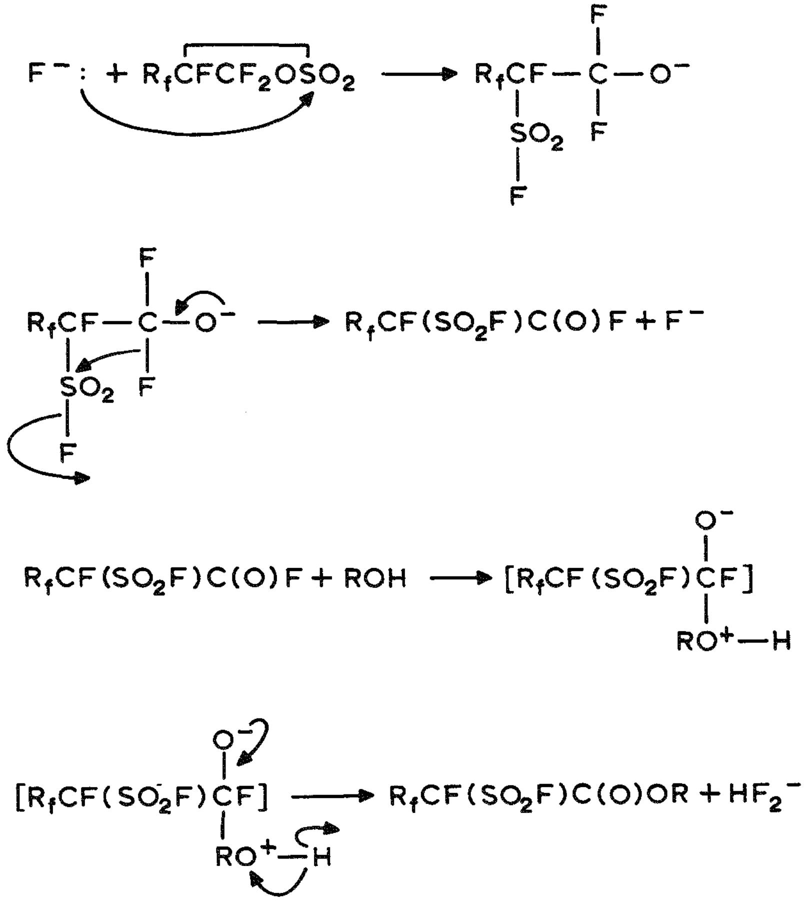
Another method for the formation of fluoroesters is the reaction between β-fluorosultones and alkoxides [11,48]:

$$\overline{CF_2CF_2OS}O_2+2R_fOM\rightarrow R_fOC(O)CF_2SO_2OR_f+2MF \tag{42}$$

$R_f=CF_3CH_2$ and $(CF_3)_2CH$, $M=Li$

$$\overline{CF_2CF_2OS}O_2+NaOCH_3\rightarrow CH_3OC(O)CF_2SO_2F+NaF \tag{43}$$

The mechanism [9,46,47] for the reaction of β-fluorosultones with alcohols proceeds in several stages. In the first stage, catalytic isomerization to the α-fluorosulfonyl fluoroalkyl carbonyl fluoride occurs. In the next stage, the FC(O) group reacts readily with alcohols (or amines, see below); the mechanism for the ester formation is:



Alternatively, one can prepare esters by using the β-fluorosultone to prepare the silver carboxylate derivative from which a number of mono/diesters can be produced [49]:

$$\overline{\mathrm{CF_2CF_2OSO_2}}+\mathrm{H_2O}\rightarrow\mathrm{FSO_2CF_2C(O)OH}+\mathrm{HF} \tag{44}$$

$$\mathrm{2FSO_2CF_2C(O)OH}+\mathrm{Ag_2O}\xrightarrow{\text{ether}}\mathrm{2FSO_2CF_2C(O)OAg}+\mathrm{H_2O} \tag{45}$$

$$\mathrm{FSO_2CF_2C(O)OAg}+\mathrm{RX}\rightarrow\mathrm{FSO_2CF_2C(O)OR}+\mathrm{AgX} \tag{46}$$

$R=CH_3,\ CH_3(CH_2)_2,\ (CH_3)_3Si,\ BrCH_2CH_2,\ CH_3CH_2C(O)OCH_2,$

$CH_2{=}CHCH_2,\ ICH_2CH_2$

With CH_2I_2 the corresponding diester, $[FSO_2CF_2C(O)O]_2CH_2$, was formed.

It should be noted that treatment of fluoroesters with SF_4/HF leads to the corresponding ethers [50]:

$$\mathrm{FSO_2CF_2C(O)OR}\xrightarrow{\mathrm{SF_4/HF}}\mathrm{FSO_2CF_2CF_2OR} \tag{47}$$

The ether product can be converted into its corresponding sulfonic acids. Thus we have a method, starting with β-fluorosultones and alcohols, that can produce a great variety of structurally modified sulfonic acids via the general pathway:

$$\overline{\mathrm{ZCXCF_2OSO_2}}\xrightarrow{\mathrm{ROH}}\mathrm{FSO_2CZXC(O)OR}\xrightarrow{\mathrm{SF_4/HF}}\mathrm{FSO_2CZXCF_2OR} \tag{48}$$

$$\mathrm{FSO_2CZXCF_2OR}\xrightarrow{\mathrm{MOH}}\mathrm{MSO_3CZXCF_2OR}\xrightarrow{\mathrm{H_2SO_4}}\mathrm{HSO_3CZXCF_2OR} \tag{49}$$

(iv) Reaction with amines

As expected, β-fluorosultones also react with a variety of amines.

$$\overline{\mathrm{ZCFCF_2OSO_2}}+\mathrm{MNu}\rightarrow\mathrm{ZCF(SO_2F)C(O)Nu}+\mathrm{MF} \tag{50}$$

$Z=F,\quad Nu=(Et)_2N,\ H_2NC(O)NH,\ C_4H_9NH,\ C_6H_5NH,\ C_6H_5N(CH_3),$

$(C_6H_5)_2N,\ \ C_8H_{17}NH,\ \overline{O(CH_2)_2NCH_2CH_2}$ [11]

$Z=F,\ CF_3,\quad Nu=C_6H_5N(CH_3)$ [11]

$M=H$

$$\overline{\mathrm{CF_2CF_2OSO_2}}+\mathrm{4HNu}\rightarrow\mathrm{NuC(O)CF_2SO_2H\cdot HNu}+\mathrm{NuC(O)CF_2SO_2Nu}+\mathrm{4HF} \tag{51}$$

Nu = p-$CH_3OC_6H_4NH$ [11]

$$\overline{CF_2CF_2OSO_2} + (CH_3)\overline{CHCH_2N(H)CH_2(CH_3)CH_2N}(H) \rightarrow (CH_3)\overline{CHCH_2N(X)CH(CH_3)CH_2N}(X) + 2HF \tag{52}$$

X = $C(O)CF_2SO_2F$ [11]

$$\overline{CFClCFClOSO_2} + (Et)_2NH \rightarrow FSO_2CFClC(O)N(Et)_2 \text{ [11]} \tag{53}$$

$$CF_3\overline{CHCF_2OSO_2} + 2HNu \rightarrow CF_3CH(SO_2Nu)C(O)Nu \tag{54}$$

Nu = $\overline{O(CH_2)_2NCH_2CH_2}$ [21]

$$C_5F_{11}\overline{CFCF_2OSO_2} + \text{xs. } NH_3 \rightarrow C_5F_{11}CF(SO_2NH_2)C(NH)NH_2 \text{ [36]} \tag{55}$$

Reaction of β-fluorosultone with ammonia can lead to formation of diamides and amidoamidines [36]. Adding NH_3 to $CF_3\overline{CFCF_2OSO_2}$ in diethyl ether at 0°C gave $FSO_2CF(CF_3)C(O)NH_2$ and NH_4F. Treatment of this amide with P_4O_{10} and heat in vacuo gave the corresponding cyanide and triazine [51].

(v) Reaction with metal fluorides

The reaction of β-fluorosultones with metal fluorides has expanded their synthetic usefulness via formation of intermediate alkoxides. In one study, $FSO_2CF_2C(O)F$ formed from $\overline{CF_2CF_2OSO_2}$ was treated with a limited amount of KF in diglyme at 40–50°C; the resulting fluoroalkoxides, $KOCF_2CF_2SO_2F$, $KOCF(CF_2SO_2F)_2$ and $KOCF(CF_2SO_2F)CF_2O(CF_2)_2SO_2F$, which formed were treated with methyl fluorosulfate and their resulting methoxy derivatives $FSO_2CF_2CF_2OCH_3$, $CH_3OCF(CF_2SO_2F)_2$, and $CH_3OCF(CF_2SO_2F)CF_2O(CF_2)_2SO_2F$ were isolated [52].

Additional fluoroalkoxides, either isolated or used as an intermediate, include $MOCF_2CF_2SO_2F$ (M = K, Cs), $MOCF_2CF(CF_3)SO_2F$ (M = K, Cs) [53], and $AgOCF_2CF_2SO_2F$ [54–58]; the isolated $MOCF_2CF_2SO_2F$ (M = K, Cs) compounds were found to be stable at room temperature but $MOCF_2CF(CF_3)SO_2F$ salts (M = K, Cs) were unstable at room temperature.

$$Z\overline{CFCF_2OSO_2} + MF \text{ (in solvent)} \rightarrow MOCF(Z)CF_2SO_2F \tag{56}$$

Z = F, M = K [53,54]

Z = F, CF_3; M = K, Cs [53]

The alkoxides are useful intermediates for preparing a number of FSO_2 precursors. The hypochlorites $ClOCF_2CFXSO_2F$, (X = F, CF_3), were prepared using ClF or $ClSO_3F$ and the corresponding alkoxides [53]. The sultones $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ with MF (M = K, Cs, and Ag) form the intermediate alkoxides that react with numerous alkyl halides [54–58]:

$$RX + \overline{CF_2CF_2OSO_2} + MF \xrightarrow{\text{Diglyme}} ROCF_2CF_2SO_2F + MX \qquad (57)$$

$R = CH_2{=}CHCH_2$, $CF_2{=}CFCH_2CH_2$, $SF_5CH_2CH_2$, $BrCH_2CH_2$,

$CH_3CH_2CH_2$, $CH_2{=}CHC(O)$ [54], $\overline{OCH_2C}HCH_2$, $(CH_3)_3SiCH_2$,

$(CF_3)_2CFCH_2CH_2$, $CH{\equiv}CCH_2$, $BrCH{=}CHCH_2$ (*cis* and *trans*), $CH_2{=}CBrCH_2$,

$(CH_3CH_2O)PF(O)CH_2CH_2$, $(CH_3CH_2O)_2P(O)CH_2CH_2$ [55]

$R = C_6H_5CH_2$, o-$(CF_3)_2C_6H_3CH_2$, $C_6F_5CH_2$ [56]

$M = K^+$, Cs^+, Ag^+; $X = Br$, Cl

$$RX_2 + 2\overline{CF_2CF_2OSO_2} + 2AgF \xrightarrow{\text{Diglyme}} R(OCF_2CF_2SO_2F)_2 + 2AgX \text{ [54]} \qquad (58)$$

$R = {-}CH_2{-}$, ${-}CH_2CH_2{-}$

$X = I$, Br

$$CF_3\overline{CFCF_2OSO_2} + AgF + RX \rightarrow ROCF_2CF(CF_3)SO_2F + AgX \qquad (59)$$

$R = CH_2{=}CHCH_2$, $CF_2{=}CFCH_2CH_2$, $(CF_3)_2CFCH_2CH_2$, CH_3,

$CH_2{=}CBrCH_2$, $SF_5CH_2CH_2$, $\overline{OCH_2C}HCH_2$,

$FSO_2CF(CF_3)CF_2OCH_2$ [57], $C_6H_5CH_2$, o-$(CF_3)_2C_6H_3CH_2$, $C_6F_5CH_2$ [56]

$X = I$, Br

It was found that the nature of the metal fluoride had an important effect on the yield of polyfluoroalkoxysulfonyl fluorides. In general, lower reaction temperatures and increased yields were obtained for the activity order $AgF \gg CsF > KF$ [54]. These reactions are carried out in two steps; the first step involves rearrangement of the fluorosultone followed by formation of the metal alkoxide. In the second step, a nucleophilic substitution of RX by $^-OCF_2CF_2SO_2F$ occurs. This mechanism is summarized as follows [54]:

$$\overline{CF_2CF_2OSO_2} \xrightarrow{MF} FC(O)CF_2SO_2F$$

$$FSO_2CF_2C(O)F + M^+F^- \rightarrow FSO_2CF_2CF_2O^-M^+$$

$$FSO_2CF_2CF_2O^-M^+ + RX \rightarrow FSO_2CF_2CF_2OR + MX$$

The β-fluorosultone $\overline{CF_2CF_2OSO_2}$ can also be used to form the useful iodo derivative octafluoro-5-iodo-3-oxapentanesulfonyl fluoride, $I(CF_2)_2O(CF_2)_2SO_2F$. It is prepared in a two-step reaction sequence [59]:

$$\overline{CF_2CF_2OSO_2} + KF \rightarrow KOCF_2CF_2SO_2F \qquad (60)$$

$$KOCF_2CF_2SO_2F + ICl + CF_2{=}CF_2 \rightarrow I(CF_2)_2O(CF_2)_2SO_2F \qquad (61)$$

This material, in the presence of benzoyl peroxide, adds to a number of alkenes and alkynes [58,59] and is an important route for the preparation of a significant number of organic sulfonyl fluorides.

Some additional MF reactions of particular interest are: the exocyclic β-fluorosultone reaction with CsF or $CsOCF_3$ to give a very stable cesium salt [7,19]:

$$F_4S{=}\overline{CCF_2OS}O_2 + CsF \text{ or } (CsOCF_3) \rightarrow Cs^+\ [SF_5C(SO_2F)COF]^- \text{ or } (COF_2) \qquad (62)$$

Treatment of $(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_3$ with CsF results in the formation of the two compounds [32]:

$$(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_3 \xrightarrow{CsF} (CF_3)_2C(O) + CF_3CF(SO_2F)C(O)F \qquad (63)$$

(vi) Reaction with metal hydroxides

β-Fluorosultones or their derivatives offer a convenient way to form fluorosulfonate salts from which the corresponding acids can be prepared.

$$Z\overline{CFCF_2OS}O_2 + MOH \rightarrow ZCF(SO_3M)C(O)OM + 2HF \qquad (64)$$

$Z = F$ [11], $CFCl_2CF_2$, $CF_2Cl(CFClCF_2)_2$, $CF_2Cl(CFClCF_2)_3$,

$CF_2Cl(CFClCF_2)_4$ [16], CF_3, C_5F_{11}[36]

$M = Li, Na, K, Sr, Ba$

$$CFCl_2CF_2\overline{CFCF_2SO_2O} \xrightarrow{NaOH(aq)} CFCl_2CFC(O)CF_2SO_3Na \text{ [16]} \qquad (65)$$

$$CF_3CCl(\overline{O)CCl(S}O_2)CF_3 \xrightarrow{NaOH(aq)} CF_3C(O)CCl(SO_3Na)CF_3 \text{ [16]} \qquad (66)$$

$$SF_5\overline{CXCF_2OS}O_2 + MOH \rightarrow SF_5CXHSO_3M\ (CO_2, HF) \qquad (67)$$

$X = F \quad M = Ca, Na$ [17]

$X = H \quad M = Ca$ [6]

The fluorosulfonate salts can be treated with sulfuric acids. In this manner, a number of structurally modified fluorosulfonic acids starting from a β-fluorosultone have been prepared [6,9,11,17,60–64]:

$HSO_3CF_2C(O)OH$, HCF_2SO_3H, CF_3CFHSO_3H, $SF_5CH_2SO_3H$,

SF_5CFHSO_3H, $SF_5CF_2SO_3H$, $(HO)_2P(O)CF_2SO_3H$,

$(HO)_2P(O)CFHSO_3H$, $(HO)_2P(O)(CF_2)_4O(CF_2)_2SO_3H$,

$R_fOCF_2CF_2SO_3H$ ($R_f = CF_3CH_2$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$),

and $CFXYCF_2O(CF_2)_2SO_3H$ ($XY = Cl_2$, HF, FH)

(vii) Other reactions

Dehydrohalogenation of appropriate *β*-fluorosultones is an effective way of generating unique FSO_2-containing ketenes [19,65]:

$$CF_3\overline{CHCF_2OSO_2} + F_3B\cdot NEt_3 \rightarrow CF_3C(SO_2F){=}C{=}O + HNEt_3\cdot BF_4 \qquad (68)$$

$$SF_5\overline{CHCF_2OSO_2} + F_3B\cdot NEt_3 \rightarrow SF_4{=}\overline{CCF_2OSO_2} + SF_5C(SO_2F){=}C{=}O$$
$$+ HNEt_3\cdot BF_4 \qquad (69)$$

In addition to preparing the $SF_5C(SO_2F){=}C{=}O$ ketene, the first cyclic example of a novel class of compounds, the alkylidenesulfur tetrafluoride, $SF_4{=}\overline{CCF_2OSO_2}$, was also prepared. This unique sultone holds promise for preparing additional *β*-fluorosultone derivatives [7,19]:

$$SF_4{=}\overline{CCF_2OSO_2} + ClF\ (CF_3OCl) \rightarrow SF_5\overline{CClCF_2OSO_2} + (COF_2) \qquad (70)$$

$$SF_4{=}\overline{CCF_2OSO_2} + HF \rightarrow SF_5\overline{CHCF_2OSO_2} \qquad (71)$$

$$SF_4{=}\overline{CCF_2OSO_2} + HCl \rightarrow SF_4Cl\overline{CHCF_2OSO_2} \qquad (72)$$

With CH_3OH and $(CH_3)_2CHOH$, the corresponding *β*-fluorosultones were produced [7]. Unfortunately, attempts at using fluoroalcohols failed [7]; with compounds such as CsF or $CsOCF_3$, the stable cesium salt, $Cs^+[SF_5C(SO_2F)COF]^-$ was formed (see eqn. (62)).

The HS and SCN derivatives of $\overline{CF_2CF_2OSO_2}$ were prepared via the following pathways [11, 12]:

$$\overline{CF_2CF_2OSO_2} + MNu \rightarrow CF_2(SO_2F)C(O)Nu + MF \qquad (73)$$

Nu = HS, SCN; M = H, Na (where Nu = SCN)

Mono- and polybasic aliphatic and aromatic acids react with *β*-fluorosultones to give mixed anhydrides which are effective acylating agents for alcohols, phenols, and thiols [1]. The reaction of *β*-fluorosultones with acyl chlorides produced derivatives of the fluoroalkenylsulfonic acid $RCF{=}CFOSO_2Cl$. For a more complete discussion that includes reaction of *β*-fluorosultones with alkyl chlorosulfates, sulfurous esters, $(RO)_2SO$, alkanesulfonyl chlorides, and phosphorus and nitrogen oxychlorides, the reader is referred to the previous reviews [1,4].

H. SPECTRAL/STRUCTURAL PROPERTIES OF THE β-FLUOROSULTONES

Since the last review, considerable progress in the structural elucidation of β-fluorosultones has occurred. Previously, a geometrical model of $\overline{CF_2CF_2OSO}_2$ was prepared on the basis of an analysis of literature values and the following structural parameters were presented [66]:

$r(S{-}C) = 1.77$ Å; $r(C{-}F) = 1.33$ Å; $r(C{-}C) = 1.45$ Å

$r(C{-}O) = 1.42$ Å; $r(S{-}O) = 1.60$ Å; $r(S{=}O) = 1.41$ Å

$\alpha(S{-}O{-}C) = 90°$; $\alpha(C{-}C{-}O) = 104°$; $\alpha(C{-}C{-}S) = 82°$; $\alpha(C{-}S{-}O) = 84°$

$\alpha(O{-}S{-}O) = 120°$; $\alpha(F{-}C{-}F) = 110°$

In 1990, the X-ray crystal structure of the first β-fluorosultone, $SF_5\overline{CHCF_2OSO}_2$, was reported [8]; as is shown in Fig. 1, the SF_5-sultone contains a four-membered sultone ring which is distorted with respect to both distance and planarity. The packing appears to be dictated by relatively strong C–H • • O hydrogen-bonding interactions between molecules (see Fig. 2) and appears to be the reason for the crystalline phase at room temperature. In Table 2, a comparison of bond angles and lengths is given for three, four-membered ring systems. For the hypothetical compound **1**, many of the reported values are assumed and in light of trends found for compounds **2** and **3**, should be re-examined. The intermolecular hydrogen bonding in $SF_5\overline{CHCF_2OSO}_2$ has all hydrogen atoms and terminal oxygen atoms involved in intermolecular attractions. Only two of the C–H • • • O distances are symmetry inequivalent, having values of 3.177 and 3.230 Å. While these distances are long

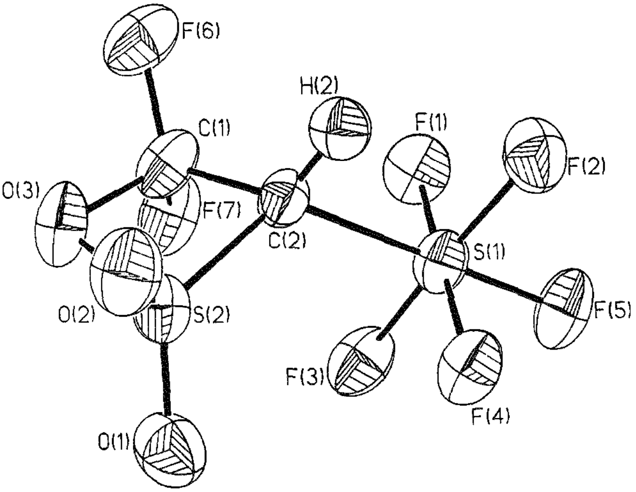


Fig. 1. Thermal ellipsoid view of $SF_5\overline{CHCF_2OSO}_2$ at 50% probability.

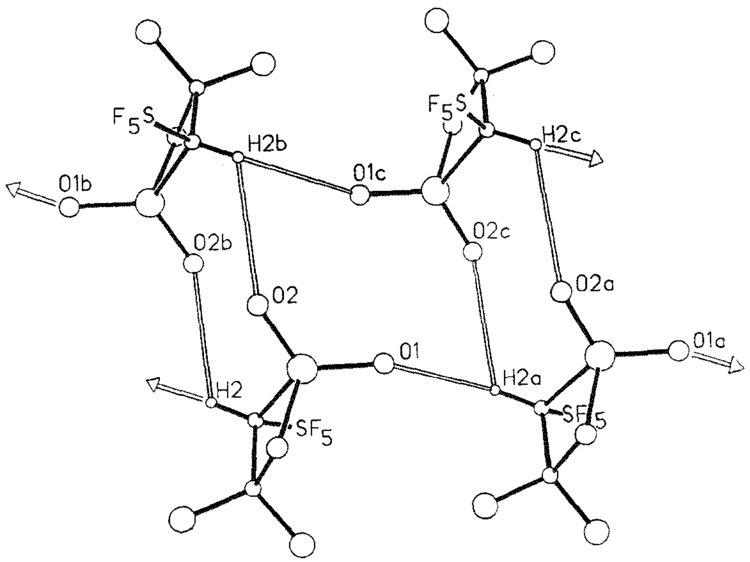


Fig. 2. Intermolecular hydrogen bonding in $SF_5\overline{CHCF_2OSO_2}$.

compared with normal interactions involving O–H and N–H groups, they are comparable with the values of 3.20 Å reported for $(HCN)_n$ [67].

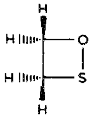
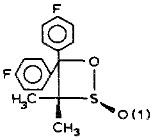
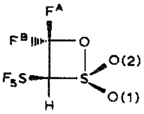
The analyses of the ^{13}C NMR spectra of some β-fluorosultones have recently been accomplished [6,7,19,34,68]. A complete listing of the chemical shifts along with respective coupling constants of β-fluorosultones are found below (see Table 5). If $\overline{CF_2CF_2OSO_2}$ is chosen as a reference, the effect of various substituents can be estimated; the corresponding increments are listed in Table 3 with regard to changes at the α carbon. The strongest shieldings are found when H replaces F or when the $F_4S{=}$ group replaces two F atoms; weaker shielding values for CF_3-, CF_3OCF_2-, and $ClCH_2CHClCH_2-$ were also found. The deshielding behavior shown by the SF_5 and SF_4Cl groups suggest high electronegativity values for these groups; respective values in Pauling units of 3.62 and 3.48 were found. All β effects were reported to be very weak [68].

The $^{13}C-^{19}F$ coupling values vary within the range of ≈270–330 Hz. These values are in good agreement with values reported for other cyclic system; for $c\text{-}C_4F_8$ and $c\text{-}C_4F_4Cl$, the corresponding values are 298 and 300 Hz, respectively [69]. A large coupling constant ($^1J_{A-1}$) increase is observed under the influence of electron withdrawal in going from $ClCH_2ClCHCH_2\overline{CFCF_2OSO_2}$ or $CF_3\overline{CFCF_2OSO_2}$ to $\overline{CF_2CF_2OSO_2}$ or $SF_5\overline{CFCF_2OSO_2}$ [68].

The IR and NMR spectral data of many β-fluorosultones show relative comparable values, i.e. in the infrared spectra the SO_2 asym stretch appears in the region 1440–1455 cm^{-1} while in the NMR spectra, the chemical shift of the $CF_{2(1,2)}(O)$ group of the sultone ring is located in the range of 80–90 ppm with coupling $J_{1,2}$

TABLE 2

Four-membered 1,2-oxathietanes

	 **1**	 **2**	 **3**
Ring bond lengths			
SO	1.669 Å	1.677(4) Å	1.621(5) Å
SC	1.81 Å[a]	1.856(4) Å	1.792(6) Å
CO	1.43 Å[a]	1.487(5) Å	1.438(8) Å
C–C	1.581 Å[a]	1.588(1) Å	1.508(8) Å
Non-ring bond lengths			
C–H	1.105 Å[a]	–	0.960 Å[a]
SO(1)	–	1.466(4) Å	1.408(5) Å
SO(2)	–	–	1.401(4) Å
Ring bond angles			
SCC	89.3°	86.4°	86.7(4)°
OCC	92.7°	93.8°	96.0(4)°
CSO	100.6°	79.0°	79.4(3)°
Dihedral	–	20.3°	14.0° 13.7°

[a] Assumed values.

TABLE 3

Substitution effect on the ^{13}C NMR chemical shifts of $\overline{CF_2CF_2OS}O_2$

Sultone	X ($X\overline{CFCF_2OS}O_2$)	Chemical shifts (ppm)	
		XCF	CF_2
$CF_3\overline{CHCF_2OS}O_2$	H	≈ −30	≈0
$CF_3\overline{CFCF_2OS}O_2$	CF_3	−13.5	−3.0
$SF_5\overline{CHCF_2OS}O_2$	H	≈ −30	≈0
$SF_5\overline{CFCF_2OS}O_2$	SF_5	+2.3	0
$SF_4Cl\overline{CHCF_2OS}O_2$	SF_4Cl	≈ +13	≈0
$CF_3OCF_2\overline{CFCF_2OS}O_2$	CF_3OCF_2	−15.1	−1.2
$CH_2ClCHClCH_2\overline{CFCF_2OS}O_2$	$CH_2ClCHClCH_2$	−7.2	+0.3
$SF_4{=}\overline{CCF_2OS}O_2$	$=SF_4$	−45.3	+1

TABLE 4
NMR data

Sultone	Chemical shifts (ppm)		Coupling constant (Hz)	Ref.
$\overline{CHFCF_{2(1,2)}OS}O_2$	CF_2	(−83.9 d,d,d, −89.4 d,d,d)	$J_{1,2}=111.5$	14
	CF	(−170.2 d,d,d)		
	CH	(6.4, d,d,d)		
$\overline{CFClCF_{2(1,2)}OS}O_2$	CF_2	(−83.9, −87.6)	$J_{1,2}=96.5$	15
	CF	(−103.0)		
$\overline{CF_{2(1,2)}CFClOS}O_2$	CF_2	(−89.7, −74.5)	$J_{1,2}=119.3$	15
	CF	(−69.0)		
$\overline{CFBrCF_{2(1,2)}OS}O_2$	CF_2	(−80.1, −87.4)	$J_{1,2}=95.6$	15
	CF	(−103.2)		
$\overline{CFICF_{2(1,2)}OS}O_2$	CF_2	(−74.0, −88.2)	$J_{1,2}=95.5$	15
	CF	(−104.8)		
$FSF_4\overline{CFCF_{2(1,2)}OS}O_2$	SF	(62.7 m), SF_4 (57.0 m)	$J_{1,2}=104.0$	17
	CF_2	(−81.2 d,p,d, −83.6 m)		
	CF	(−116.9 m)		
$SF_5\overline{CHCF_{2(1,2)}OS}O_2$	SF_5	(69.4 m)	$J_{1,2}=103.0$	6
	CF_2	(−72.8 d, −79.7 d)		
	CH	(6.58 m)		
$SF_4Cl\overline{CHCF_{2(1,2)}OS}O_2$	SF_4	(67 m, 120 m, 141.7 m)	$J_{1,2}=100.8$	19
	CF_2	(−74.9 d, −78.9 d,m)		
	CH	(7.1 m)		
$SF_4{=}\overline{CCF_2OS}O_2$	SF_4	(40.9, 47.2, 51.9)	–	19
	CF_2	(−76.3)		
$FSO_2\overline{CHCF_2OS}O_2$	SO_2F	(68.1 m), CF_2 (−60.2 m)	–	20
	CH	(4.42 m)		
$\overline{CF_2CF_2OS}O_2$	CF_2	(−93.3 m, −102.6 m)	–	11,14,53

$CF_3\overline{CHCF_{2(1,2)}OS}O_2$	CF_3 CH	(−64.5 m), CF_2 (−76.9 d,q) (5.6 t,q)	$J_{1,2}=103.9$	21
$C_2H_5O\overline{C(CF_3)CF_{2(1,2)}SO_2O}$	CF_3 CF_2	(−77.6 d) (−94.6 d, −100.5 d,q)	$J_{1,2}=173$	26
$CF_3\overline{CFCF_{2(1,2)}OS}O_2$	CF_2 CF_3	(−82.4 m, −88.6 m) (−74.4 d,t,m), CF (−153.1 d,q)	$J_{1,2}=107.2$	53
$(CF_3)_2\overline{CCF_2OS}O_2$	CF_3 CF_2	(−62.0) (−76.3)	–	22
$HCF_2CF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2(O) CF_2 CF	(−82.7 m, −85.6 m) (−122.2 m), HCF_2 (−137.9 m) (−151.1 m), CH (6.2 t,t)	$J_{1,2}=100.1$	24
$CF_2ClCF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2(O) CF_2Cl CF	(−81.6 m, −84.4 m) (−86.3 m), CF_2 (−114.6 m) (−149.3 m)	$J_{1,2}=107.0$	24
$CF_3CF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2 CF_3 CF	(−82.6 m, −85.9 m) (−80.7 d,d), CF_2 (−121.0 m) (151.3 m)	$J_{1,2}=109.0$	24
$CF_2ClCFClCF_2\overline{CFCF_2OS}O_2$	CF_2Cl CF_2 CF(S)	(−64), CF_2(O) (−83.0) (−109), CFCl (−128) (−148)	–	31
$CH_2ClCHClCH_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2 CF CH_2Cl	(−82.3 d,d, −86.8 d,d) (−145.3 d,m), CH_2 (3.6 m) (4.2 m), CH (4.8 m)	$J_{1,2}=107.2$	34
$CF_3OCF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_3 CF_2 CF	(−57.3 t), CF_2C (−80.7 m) (−85.4 d, d, t, −90.6 d, t) (−153.9 d, t)	$J_{1,2}=112.9$	27
$CF_3OCF_2CF_2OCF_2\overline{CFCF_{2(1,2)})OS}O_2$	CF_3 CF_2(O) CF_2CF OCF_2	(−58.4 t) (−85.3 d,d,t, −91.7 d,t) (−79.5 m), CF_2O (−90.9 m) (−93.2 q), CF (−154.7 d,t)	$J_{1,2}=112.9$	27

TABLE 4 (*continued*)

Sultone	Chemical shifts (ppm)		Coupling constant (Hz)	Ref.
$CF_3(CF_2)_2CF_2O\overline{CFCF_{2(1,2)}SO_2O}$	CF_3	(−84.5 t)	$J_{1,2}=153.3$	30
	$CF_2(S)$	(−84.2 d,m, −87.0 d,m)		
	CF_2O	(−100.6 d,m, −102.8 d.m)		
	CF	(−91.8 m), $(CF_2)_2$ (−129.5 m)		
$(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_3$	CF_3	(−73.6 d,d), $(CF_3)_2$ (−80.5 m)	–	32
	CF(O)	(−83.7 m), CFO (−143.1 d,m)		
	CF(S)	(−149.6 d,q)		
$CF_3CF_2CF_2O\overline{CFCF_{2(1,2)}SO_2O}$	CF_3	(−83.5 t)	$J_{1,2}=151.0$	26
	$CF_2(O)$	(−84.1 m, −86.5 m)		
	CF_2O	(−99.8 m, −101.2 m)		
	CF	(−90.3 m), CF_2 (−131.4 s)		
$(CF_3)_2CFOCF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_3	(−81.3 m)	$J_{1,2}=108.0$	33
	$CF_2(O)$	(−82.4 d,d,t, −89.5 d,t)		
	OCF_2	(−74.6 m), CFO (−145.7 t, sep)		
	CF	(−151.8 t,d)		
$(CF_3)_2CFOCF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_3	(−80.6 br.s)	$J_{1,2}=109.0$	32
	$CF_2(O)$	(−83.3 d,d,t, −89.0 d,t)		
	OCF_2	(−73.9 m), CFO (−144.4 t,m)		
	CF	(−151.3 d,t)		
$(CF_3)_2CFOCF(\overline{O)CF(S}O_2)CF_2OSO_2F$	SO_2F	(51.2 m)	–	33
	CF_2	(−77.1, AB center), CF(O) (−77.6 m)		
	CF_3	(−80.9 m), CF (−145.2 d, sep)		
	CF(S)	(−149.0 t,d)		
$CF_3(CF_2)_2CF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_3	(−81.2 t,t)	$J_{1,2}=104.9$	24
	$CF_2(O)$	(−82.6 m, −85.5 m)		
	$(CF_2)_2$	(−116.7 m, −126.2 m)		
	CF_2	(−120.2 m), CF (−151.2 m)		

$CF_3(CF_2)_2CF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_3	(−81.4 m)	–	35
	$CF_2(O)$	(−82.4 d,m, −86.4 d,m)		
	$(CF_2)_2$	(−119.7 m, −116.6 m)		
	CF_2	(−125.6 m), CF (−151.2 m)		
$C_6F_5CF_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2O	(−80.8 d,m, −87.6 d,m)	$J_{1,2} = 109$	35
	CF_2	(−94.0 m, −97.2 m)		
	CF	(−136.6 m)		
	C_6F_5	(−137.5 m, −145.4 m, −163.5 m)		
$F_2C{=}CFCF_2\overline{CFCF_{2(1,2)}OS}O_2$	$CF_2(O)$	(−81.4 m, AB center)	–	29
	$CF_2{=}$	(−88.7 d,d,t, −105.1 d,t,t)		
	CF_2	(−114.3 m), CF (−147.1 d,d,t)		
	=(CF)	(190.6 d,d,t)		
$CF_2{=}CF(CF_2)_2\overline{CFCF_{2(1,2)}OS}O_2$	CF_2	(−84.5 d,t, −87.7 d,d,t)	$J_{1,2} = 110.1$	37
	$CF_2{=}$	(−89.3 d,d,t, −106.5 d,d,t,t)		
	$(CF_2)_2$	(−119.9 d,d,m, −118.0 m)		
	CF	(−152.9 m), CF= (−192.8 d,d,m)		
$[CF_2CF(\overline{SO_2)CF_{2(1,2)}(O})]_2$	$CF_2(O)$	(−84.0 d,t, −86.7 d,m)	$J_{1,2} = 110.8$	37
	CF_2	(−116.3 d,m), CF (−153.4 m)		
$F_2C{=}CF(CF_2)_4\overline{CFCF_{2(1,2)}OS}O_2$	$CF_2(O)$	(−83.6 m, AB center)	$J_{1,2} = 108.0$	38
	$CF_2{=}$	(−87.9 d,d,t, 105.1 d,d,t)		
	$(CF_2)_4$	(−115.9 m −117.4 m)		
	$(CF_2)_4$	(−119.0 m −122.6 m)		
	CF	(−149.9 m), =CF (−189.7 m)		
$[CF_{2(1,2)}(\overline{O)CF(S}O_2)CF_2CF_2]_2$	$CF_2(O)$	(−83.2 m, AB center)	$J_{1,2} = 107.2$	38
	$(CF_2)_2$	(−115.5 m, −118.4 m)		
	CF	(−150.2 m)		

TABLE 5

^{13}C NMR data

Sultone	Chemical shifts (ppm)		Coupling constant (Hz)	Ref.
$FSF_4\overline{CHC_{(2)}F_{2(1)}OS}O_2$	CH	(99.6 d,p,m)	$J_{1,2}=293.0$	6
	CF_2	(112 br.p)		
$SF_4Cl\overline{CHC_{(2)}F_{2(1)}OS}O_2$	CF_2	(113.4 t)	$J_{1,2}=294.0$	19
	CH	(108.8 d,m)		
$SF_4{=}\overline{CC_{(2)}F_{2(1)}OS}O_2$	=C	(80.7 $\approx$p,t)	$J_{1,2}=282.4$	19
	CF_2	(114.5 d,t)		
$\overline{CF_2C_{(2)}F_{2(1)}OS}O_2$	CF_2	(126.0 t,t)	$J_{1,2}=294.3$	68
	CF_2O	(113.5 t,t)		
$CF_3\overline{CFC_{(2)}F_{2(1)}OS}O_2$	CF_3	(117.2 q,d,m)	$J_{1,2}=293.6$	68
	CF	(112.5 d,m)		
	CF_2	(110.5 t,d)		
$CF_3\overline{CHC_{(2)}F_{2(1)}OS}O_2$	CF_3	(118.4 q)	$J_{1,2}=291.0$	68
	CH	(79.3 q,d,d)		
	CF_2	(111.2 t,q)		
$FSF_4\overline{CFC_{(2)}F_{2(1)}OS}O_2$	CF	(128.3 d,m)	$J_{1,2}=298.0$	68
	CF_2	(113.5 t,p)		
$CF_3OCF_2\overline{CFC_{(2)}F_{2(1)}OS}O_2$	CF_3	(119.2 q,m)	$J_{1,2}=294.0$	68
	OCF_2	(114.7 m)		
	CF_2	(112.3 d,d,m)		
	CF	(110.9 d,m)		
$C'H_2ClCHClCH_2\overline{CFC_{(2)}F_{2(1)}OS}O_2$	CF_2	(113.8 d,d,d)	$J_{1,2}=290.0$	34
	CF	(118.9 d,d,d)		
	CH_2	(32.4 d), CH (51.7 s)		
	$C'H_2$	(46.8 s)		

TABLE 6
MS data

Sultone	Fragment ions (*m*/*e*)	Ref.
$SF_5CFCF_2OSO_2$	208 $(M-SO_3)^+$, 161 $(M-SF_5)^+$, 129 $(CF(SO)CF_2)^+$, 127 $(SF_5)^+$, 113 $(CF(S)CF_2)^+$, 97 $(CFCF_2O)^+$, 81 $(CFCF_2)^+$, 80 $(SO_3)^+$, 66 $(CF_2O)^+$, 64 $(SO_2)^+$, 51 $(SF)^+$, 48 $(SO)^+$	17
$SF_5CHCF_2OSO_2$	269 $(M-H)^-$, 142 $(CCF_2OSO_2)^-$, 127 $(SF_5)^-$, 123 $(CCFSO_3)^-$, 83 $(SF_2CH)^-$, 79 $(CHCF_2O)^-$	6
$SF_4{=}CCF_2OSO_2$	250 $(M)^+$, 170 $(M-SO_3)^+$, 165 $(SF_3CSO_2)^+$, 151 $(M-SO_3F)^+$, 94 $(C_2F_2S)^+$, 89 $(SF_3)^+$, 70 $(SF_2)^+$, 64 $(SO_2)^+$, 51 $(SF)^+$	7
$SF_4ClCHCF_2OSO_2$	269 $(M-O)^-$, 167 $(M-HCl, SO_2F)^-$, 142 $(M-HCl, SF_4)^-$, 120 $(SF_4C)^-$, 108 $(SF_4)^-$, 101 $(CSF_3)^-$, 89 $(SF_3)^-$, 70 $(SF_2)^-$	7
$CH_2ClCHClCH_2CFCF_2OSO_2$	239 $(M-^{37}Cl)^+$, 237 $(M-^{35}Cl)^+$, 161 $(CF(SO_2)CF_2(O))^+$, 142 $(CF_2CSO_3)^+$, 108 $(CF_2CFC_2H_3)^+$, 95 $(CFSO_2)^+$, 80 $(SO_3)^+$, 64 $(SO_2)^+$, 62 $(CCF_2)^+$	34
$CF_3OCF_2CFCF_2OSO_2$	297 $(MH)^+$, 277 $(MH-HF)^+$, 216 $(M-SO_3)^+$, 211 $(M-CF_3O)^+$, 179 $(CF_3OCF_2CS)^+$, 145 $(CF(SO_2)CF_2)^+$, 128 $(CF_2OCFC)^+$, 95 $(CFSO_2)^+$, 80 $(SO_3)^+$, 69 $(CF_3)^+$, 64 $(SO_2)^+$	27
$CF_3O(CF_2)_2OCF_2CFCF_2OSO_2$	413 $(MH)^+$, 393 $(M-F)^+$, 332 $(M-SO_3)^+$, 327 $(M-CF_3O)^+$, 185 $(CF_3OCF_2CF_2)^+$, 163 $(CF_3OCFCFO)^+$, 135 $(CF_3OCF_2)^+$, 129 $(CF(SO)CF_2)^+$, 100 $(CF_2CF_2)^+$, 95 $(CFSO_2)^+$, 79 $(CFSO)^+$, 69 $(CF_3)^+$, 64 $(SO_2)^+$	27
$CF_3(CF_2)_2CF_2OCFCF_2SO_2O$	397 $(MH)^+$, 316 $(M-SO_3)^+$, 263 $(M-CF_2SO_2F)^+$, 225 $(C_4F_7OCO)^+$, 219 $(C_4F_9)^+$, 177 $(OCF(O)CF_2SO_2)^+$, 169 $(C_3F_7)^+$, 113 $(CFCF_2S)^+$, 78 $(CF_2CO)^+$, 69 $(CF_3)^+$, 64 $(SO_2)^+$, 63 $(CFS)^+$	30

TABLE 6 (*continued*)

Sultone	Fragment ions (*m*/*e*)	Ref.
$CF_2{=}CF(CF_2)_2\overline{CFCF_2OSO_2}$	342 $(M)^+$, 323 $(M{-}F)^+$, 231 $(C_5F_9)^+$, 212 $(C_5F_8)^+$, 193 $(M{-}CF_3SO_3)^+$, 155 $(C_5F_5)^+$, 109 $(C_3F_3O)^+$, 95 $(CFSO_2)^+$, 79 $(CFSO)^+$, 64 $(SO_2)^+$, 48 $(SO)^+$, 47 $(CFO)^+$, 44 $(CS)^+$	37
$[CF_2(\overline{O)CF(S}O_2)CF_2]_2$	423 $(MH)^+$, 403 $(M{-}F)^+$, 342 $(M{-}SO_3)^+$, 259 $(C_6F_9O)^+$, 231 $(C_6F_5SO_2)^+$, 181 $(C_4F_7)^+$, 169 $(C_4F_3SO_2)^+$, 143 $(C_4F_5)^+$, 95 $(CFSO_2)^+$, 81 $(C_2F_3)^+$, 79 $(CFSO)^+$, 66 $(CF_2O)^+$, 64 $(SO_2)^+$, 63 $(CFS)^+$	37

values of 100–110 Hz. Knowledge of these spectral characteristics is necessary in order to determine the structures of new β-sultones. A complete listing of known spectral values including IR, NMR, and MS data are given in Tables 1 and 4–6. The ^{19}F NMR chemical shifts of the β-sultones are reported relative to F-11 ($CFCl_3$) for ^1H and ^{13}C NMR relative to TMS ($(CH_3)_4Si$).

I. USES OF THE β-FLUOROSULTONES

One of the principal uses found for β-fluorosultones is in the preparation of mono-, poly-, and polymeric fluoroalkyl sulfonic acids. In particular, the preparation and uses for the polymer sulfonic acid called Nafion has gained considerable attention. Nafion (Du Pont) is prepared from $\overline{CF_2CF_2OSO_2}$ via the following sequence [70,71]:

$$\overline{CF_2CF_2OSO_2} \xrightarrow{F^-} FC(O)CF_2SO_2F$$

$$CF_3\overline{CFCF_2O} + FC(O)CF_2SO_2F \xrightarrow{F^-} FC(O)CF(CF_3)OCF_2CF_2SO_2F$$

$$FC(O)CF(CF_3)OCF_2CF_2SO_2F + nCF_3\overline{CFCF_2O} \xrightarrow{F^-} FC(O)CF(CF_3)(OCF_2CF(CF_3))_nOCF_2CF_2SO_2F$$

$$FC(O)CF(CF_3)(OCF_2CF(CF_3))_nOCF_2CF_2SO_2F + Na_2CO_3 \xrightarrow{F^-} CF_2{=}CF(OCF_2CF(CF_3))_nOCF_2CF_2SO_2F \text{ (PSEPVE)}$$

The polymeric material (PSEPVE) is copolymerized with $CF_2{=}CF_2$ to form a polymeric resin which can be melted and shaped by conventional methods. It can also be converted by base/acid treatment to the corresponding free sulfonic acid called Nafion. Nafion membranes are useful as separators for electrochemical and chemical processing [70,71]*. It has also been shown to be useful as a fuel cell electrolyte [72] and catalyst in organic synthesis [73].

A series of partially fluorinated sulfonyl fluoride-containing polymers has also been prepared by reaction of β-fluorosultones: $\overline{CF_2CF_2OS}O_2$, $CF_3\overline{CFCF_2OS}O_2$, $SF_5\overline{CFCF_2OS}O_2$, and $SF_5\overline{CHCF_2OS}O_2$ with polyvinyl and allyl alcohols [46].

A number of fluorocarbon vinyl sulfonyl fluorides of the type $CF_2{=}CF(CFR)_nCFHSO_2F$ where $R = F$ or perfluoroalkyl group and $n = 1$–5 or of the type $ROCF_2CFXSO_2F$ where $X = F$, CF_3 and $R = \overline{OCH_2C}HCH_2$, $HC{\equiv}CCH_2$, $H_2C{=}CHCH_2$, $F_2C{=}CF(CH_2)_2$ have been reported [31,54,55,57]. These materials should be useful comonomers with other fluoro-olefins such as $CF_2{=}CF_2$ in the preparation of polymers with ion-exchange capabilities.

Copolymerization of $CF_2{=}CFSO_2F$ (formed from $CF_3\overline{CFCF_2OS}O_2$) with fluoro-olefins also leads to the production of stable fluorinated ion-exchange resin [74]. A number of additional polymeric materials have been prepared from β-fluorosultones and it is expected that, in this area, extensive use of β-fluorosultones will be found.

In addition to the work dealing with Nafion and other polymeric sulfonic acids or polymeric precursors, a number of important monosulfonic acids have been prepared from sultones, i.e. $(HO)_2P(O)CF_2SO_3H$ and $SF_5CF_2SO_3H$ [61,63,64]. The $SF_5CF_2SO_3H$ acid is an analogue to triflic acid (CF_3SO_3H).

Biological activity has also been reported for a number of derivatives prepared from β-fluorosultones [75]. Another proposed use of β-fluorosultones is as a stabilizer for liquid SO_3 [76].

The ability of the β-fluorosultones to form a large number of structurally modified mono-, poly-, and polymeric fluoroalkylsulfonic acids and precursors is unique and will continue to play an important role in the development of this important class of compounds.

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*For good reviews of the structure, chemistry and uses of Nafion, see refs. 70(c) and 70(d).

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