

## $\beta$ -Fluorosultones: synthesis, reactivity, structure and uses

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### A. ABSTRACT

$\beta$ -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

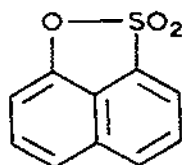
[1,2]. As in the case of lactones, there are  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -sultones along with a large number of cyclic sulfonates. Among the unsubstituted compounds, the  $\gamma$ - and  $\delta$ -sultones are the most stable and contain five- and six-membered rings, respectively.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

Sulfur trioxide reacts with fluoro-olefins to give stable  $\beta$ -sultones; but with some fluoro-olefins such as tetrafluoroethylene, the final products include a  $\beta$ -sultone,  $\text{CF}_2\text{CF}_2\text{OSO}_2$ , and a  $\beta$ -disultone,  $\text{CF}_2\text{CF}_2\text{OSO}_2\text{OSO}_2$ ; also mentioned is an eight-membered ring heterocycle,  $(\text{CF}_2)_2\text{OSO}_2(\text{CF}_2)_2\text{OSO}_2$  [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  $\beta$ -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 $\beta$ -FLUOROSULTONES

The first non-fluorinated  $\beta$ -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  $\beta$ -fluorosultones prepared was 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone,  $\text{CF}_3\text{CF}(\text{OH})\text{CF}_2\text{OSO}_2$ . This  $\beta$ -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  $\beta$ -fluorosultones have been prepared.

#### D. PROPERTIES OF $\beta$ -FLUOROSULTONES

Generally, fluorinated  $\beta$ -sultones are thermally stable, colorless liquids which usually fume in air. They dissolve in saturated hydrocarbons, in fluoro- and chloro-hydrocarbons, and in polyhalogeno-olefins. While  $\beta$ -fluorosultones in general are covalent liquids at room temperature, it is surprising to find that the  $\beta$ -fluorosultone  $\text{SF}_5\text{CHCF}_2\text{OSO}_2$  exists as a solid [6]; only one other  $\beta$ -fluorosultone,

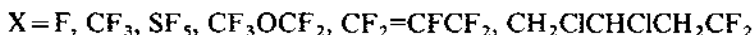
$\text{SF}_4(\text{OCH}_3)\overline{\text{CHCF}_2\text{OSO}_2}$ , is a solid at room temperature [7]. The crystal structure of  $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$  has been determined [8].

Fluorosultones react with water and many inorganic or organic compounds containing  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SCN}$ , and  $-\text{SH}$  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].

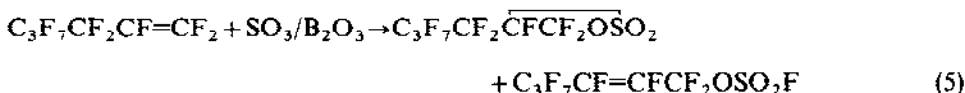
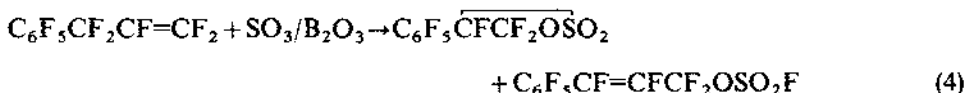
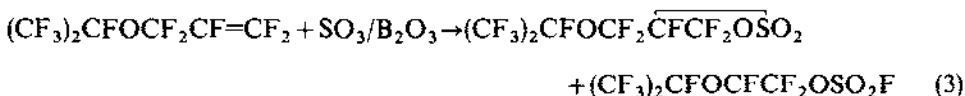
In Table 1, a complete list of known  $\beta$ -fluorosultones along with their respective melting or boiling points and IR data is reported.

#### E. PREPARATION OF $\beta$ -FLUOROSULTONES

The synthesis of  $\beta$ -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,  $\text{SO}_3(\text{m})$ , which reacts with fluoro-olefins:



The generation and handling of monomeric  $\text{SO}_3$  can be accomplished in several ways. In one method, trimeric  $\text{SO}_3$ ,  $\text{SO}_3(\text{t})$ , 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  $\text{SO}_3(\text{m})$  in situ; since the  $\text{SO}_3(\text{t})$  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  $\text{SO}_3$ . Impurities such as water can lower the overall yield of the sultone or produce side products. In particular, with the impurities  $\text{B}_2\text{O}_3$ ,  $\text{BF}_3$ , or  $\text{B}(\text{OCH}_3)_3$ , the following reactions have been observed [32,35,40]:



A method of preparing the  $\beta$ -fluorosultone  $\text{CF}_3\overline{\text{CFC}(\text{CF}_3)_2\text{OSO}_2}$ , involves the

TABLE I  
β-Fluorosultones

| Sultone                                                     | BP/IR (cm <sup>-1</sup> ) <sup>a</sup>                                                                                                                 | Ref.       |
|-------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$             | 42°C<br>SO <sub>2</sub> (asym, 1451; sym, 1235)<br>CF <sup>+</sup> (1030-1090)                                                                         | 10-14      |
| $\overline{\text{CFBrCF}_2\text{OSO}_2}$                    |                                                                                                                                                        | 15         |
| $\left\{ \overline{\text{CFClCF}_2\text{OSO}_2}^b \right\}$ | {mixture<br>73-77°C                                                                                                                                    | 5,10,11,16 |
| $\overline{\text{CF}_2\text{CFClOSO}_2}^b$                  | 110-113°C                                                                                                                                              | 11         |
| $\overline{\text{CFClCFClOSO}_2}$                           | 110-112°C                                                                                                                                              | 11         |
| $\overline{\text{CCl}_2\text{CF}_2\text{OSO}_2}$            | 88°C                                                                                                                                                   | 17,18      |
| $\overline{\text{SF}_5\text{CF}_2\text{CF}_2\text{OSO}_2}$  | SO <sub>2</sub> (asym, 1448; sym, 1214)<br>CF (1020-1096)<br>SF <sup>+</sup> (stret, 854-896; def, 596)                                                |            |
| $\overline{\text{SF}_5\text{CHCF}_2\text{OSO}_2}$           | 108-111°C/600 mm; m.p. 47-48°C<br>SO <sub>2</sub> (asym, 1419; sym, 1203)<br>CF <sup>+</sup> (1078-1106)<br>SF <sup>+</sup> (stret, 819-878; def, 612) | 18,6       |
| $\overline{\text{SF}_5\text{CClCF}_2\text{OSO}_2}$          |                                                                                                                                                        | 7          |
| $\overline{\text{SF}_4=\text{CCF}_2\text{OSO}_2}$           | SO <sub>2</sub> (asym, 1415; sym, 1192-1235)<br>SF <sup>+</sup> (stretching, 857-874)                                                                  | 19         |
| $\overline{\text{ClSF}_4\text{CHCF}_2\text{OSO}_2}$         | SO <sub>2</sub> (asym, 1430; sym, 1214);<br>SF <sup>+</sup> (stretching, 814-853)                                                                      | 19         |

|                                                                                               |                                                                              |                |
|-----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------|
| $\text{SF}_4(\text{OCH})_3\overline{\text{CHCF}_2\text{OSO}_2}$                               | m.p. 21°C                                                                    | 7              |
| $\text{SF}_4\text{OCH}(\text{CH}_3)_2\overline{\text{CHCF}_2\text{OSO}_2}^s$                  | -                                                                            | 7              |
| $\overline{\text{CHF}\text{CF}_2\text{OSO}_2}$                                                | 97°C<br>SO <sub>2</sub> (asym, 1455; sym, 1239)<br>CF (1050-1129); CH (2890) | 10, 11, 13, 14 |
| $\text{FSO}_2\overline{\text{CHCF}_2\text{OSO}_2}$                                            | 49-51°C/15 mm                                                                | 20             |
| $\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                                                 | -                                                                            | 15             |
| $\text{CF}_3\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                                      | 46.5°C<br>SO <sub>2</sub> (asym, 1455; sym, 1237)<br>CF (1005-1340)          | 10-14          |
| $\text{CF}_3\overline{\text{CHCF}_2\text{OSO}_2}$                                             | 92°C                                                                         | 21             |
| $(\text{CF}_3)_2\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                                  | 63°C                                                                         | 22             |
| $\text{CH}_3\text{O}\overline{\text{CF}\text{CF}\text{CF}\text{SO}_2\text{O}}$                | 39-40°C/3 mm                                                                 | 23             |
| $\text{C}_2\text{F}_5\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                             | 66°C                                                                         | 24             |
| $\text{CF}_2\text{ClCF}_2\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                         | 103°C                                                                        | 24             |
| $\text{CFCl}_2\text{CF}_2\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                         | 129-131.5°C                                                                  | 5, 16          |
| $\text{CF}_2\text{HCF}_2\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                          | 90°C                                                                         | 24             |
| $(\text{CF}_3)_2\overline{\text{CF}\text{CF}(\text{CF}_3)\text{SO}_2\text{O}}$                | -                                                                            | 25             |
| $\text{C}_2\text{H}_5\text{O}\overline{\text{CF}(\text{CF}_3)\text{CF}_2\text{SO}_2\text{O}}$ | -                                                                            | 26             |
| $\text{C}_2\text{H}_5\text{O}\overline{\text{CF}\text{CF}\text{CF}\text{ClSO}_2\text{O}}$     | 41-42°C/3 mm                                                                 | 23             |
| $\text{CF}_3\text{C}\overline{\text{Cl}(\text{O})\text{CCl}(\text{SO}_2)\text{CF}_3}$         | 132-133.8°C                                                                  | 5, 16          |
| $\text{CF}_3\text{OCF}_2\overline{\text{CF}\text{CF}_2\text{OSO}_2}$                          | 69-72°C<br>SO <sub>2</sub> (asym, 1446; sym, 1249)                           | 27             |

TABLE I (continued)

| Sultone                                                                                                     | BP/IR (cm <sup>-1</sup> ) <sup>a</sup>                                                                      | Ref.  |
|-------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-------|
| CF <sub>2</sub> =CF $\overline{\text{CFCF}_2\text{SO}_2\text{O}}$                                           | 22.5–23°C/30 mm                                                                                             | 28    |
| CF <sub>2</sub> =CF $\overline{\text{CF}_2\text{CFCF}_2\text{OSO}_2}$                                       | 100–102°C<br>SO <sub>2</sub> (asym, 1450); CF <sub>2</sub> =CF (1795)                                       | 29    |
| C <sub>3</sub> F <sub>7</sub> O $\overline{\text{CFCF}_2\text{SO}_2\text{O}}$                               | 66°C/180 mm                                                                                                 | 26    |
| C <sub>4</sub> F <sub>9</sub> O $\overline{\text{CFCF}_2\text{SO}_2\text{O}}$                               | 85–90°C/197 mm<br>SO <sub>2</sub> (asym, 1449; sym, 1221)                                                   | 30    |
| CF <sub>2</sub> ClCFClCF <sub>2</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                                | 55°C/25 mm<br>SO <sub>2</sub> (asym, 1440)                                                                  | 5,31  |
| (CF <sub>3</sub> ) <sub>2</sub> CFOCF(O) $\overline{\text{CF}(\text{SO}_2)\text{CF}_3}$                     | 105–107°C                                                                                                   | 32    |
| (CF <sub>3</sub> ) <sub>2</sub> CFOCF <sub>2</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                   | 107–109°C<br>SO <sub>2</sub> (asym, 1445)                                                                   | 32,33 |
| CF <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$    | 88°C/336 mm<br>SO <sub>2</sub> (asym, 1449; sym, 1225)                                                      | 27    |
| (CF <sub>3</sub> ) <sub>2</sub> CFOCF(O) $\overline{\text{CF}(\text{SO}_2)\text{CF}_2\text{OSO}_2\text{F}}$ | 51°C/5 mm<br>SO <sub>2</sub> (asym, 1445); CF, CO, SO <sub>2</sub> (1100–1300)<br>OSO <sub>2</sub> F (1490) | 33    |
| CH <sub>2</sub> ClCHClCH <sub>2</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                                | 65–68°C/10 mm<br>SO <sub>2</sub> (asym, 1413; sym, 1203)<br>CF (1059–1300)                                  | 34    |
| C <sub>4</sub> F <sub>9</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                                        | 114°C                                                                                                       | 24,35 |
| C <sub>4</sub> H <sub>9</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                                        | 63–65°C/20 mm                                                                                               | 11    |
| C <sub>5</sub> F <sub>11</sub> $\overline{\text{CFCF}_2\text{OSO}_2}$                                       | 134–136.5°C<br>SO <sub>2</sub> (asym, 1450)                                                                 | 36    |

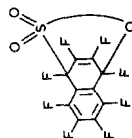
|                                                                                      |                                                                                                         |       |
|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|-------|
| $\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_2\overline{\text{CFCF}_2\text{OSO}_2}$ | 56–58°C/0.22 mm                                                                                         | 5,16  |
| $\text{H}(\text{CF}_2)_6\overline{\text{CFCF}_2\text{OSO}_2}$                        | 76°C/22 mm                                                                                              | 11    |
| $\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_3\overline{\text{CFCF}_2\text{OSO}_2}$ | 81–82°C/0.08 mm                                                                                         | 5,16  |
| $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$           | 115°C (est.), 79 ± 1°C/226 mm<br>SO <sub>2</sub> (asym, 1441; syn, 1216)<br>CF <sub>2</sub> = CF (1785) | 31,37 |
| $\text{CF}_2=\text{CF}(\text{CF}_2)_4\overline{\text{CFCF}_2\text{OSO}_2}$           | 62–63°C/15 mm                                                                                           | 38    |
| $[\text{CF}_2(\text{O})\overline{\text{CF}(\text{SO}_2)\text{CF}_2}]_2$              | 69 ± 1°C/15 mm<br>SO <sub>2</sub> (asym, 1441; sym, 1216)                                               | 37    |
| $[\text{CF}_2(\text{O})\overline{\text{CF}(\text{SO}_2)(\text{CF}_2)_2}]_2$          | 91–92°C/15 mm                                                                                           | 38    |
| $\text{C}_6\text{F}_5\text{CF}_2\overline{\text{CFCF}_2\text{OSO}_2}$                | –                                                                                                       | 35    |
| $\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_4\overline{\text{CFCF}_2\text{OSO}_2}$ | 115–116°C/0.4 mm                                                                                        | 5,16  |
| $\text{c-C}_{10}\text{F}_8\text{OSO}_2^{\text{d}}$                                   | –                                                                                                       | 39    |

<sup>a</sup> 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<sup>-1</sup> region.

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

<sup>c</sup> This sultone is stable in solution [7].

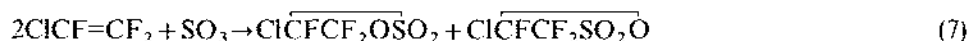
<sup>d</sup> Since the chemical composition is not verified, this material may be a pyrosulfate [4].



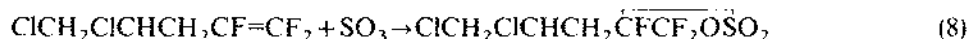
reaction of  $\text{CF}_3\text{CFHSO}_2\text{F}$  with  $\text{Me}_3\text{N-SiF}_4$  in the presence of  $(\text{CF}_3)_2\text{C=O}$ . Extension of this procedure has supposedly yielded a series of  $\beta$ -fluorosultones [25].

It has been reported that reaction of hexafluoroisobutylenic 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  $\text{R}_f\text{OCF=CF}_2$  ( $\text{R}_f = \text{C}_3\text{F}_7$ , and  $\text{C}_4\text{F}_9$ ) and  $\text{ClCF=CF}_2$ -type olefins, the following products have been reported [11,26,30]:

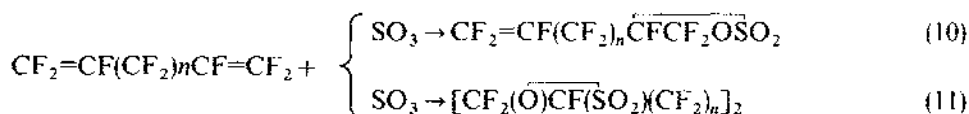
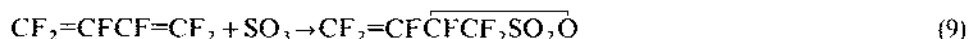


Substitution of hydrogen on the carbon which is part of the double bond, can also affect the yield and product distribution. A decreasing tendency toward formation of  $\beta$ -fluorosultones was found for  $\text{CF}_2=\text{CF}_2$ ,  $\text{CFH=CF}_2$ , and  $\text{CH}_2=\text{CF}_2$ ; byproducts were thought to be the corresponding cyclic sulfonate-sulfate anhydrides. In the case of  $\text{CF}_2=\text{CFH}$ , the resulting byproduct is  $\text{CF}_2\text{CHFSO}_2\text{OSO}_2\text{O}$  [11]. It is possible to substitute hydrogen in positions other than at the olefinic carbon and obtain the desired  $\beta$ -fluorosultones [34].



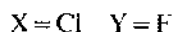
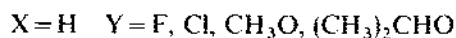
However, the presence of hydrogen in the chain requires lower temperatures in order to prevent attack by  $\text{SO}_3(\text{m})$  on C-H bonds.

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



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

More recently, the synthesis of the exocyclic  $\beta$ -fluorosultone  $\text{F}_4\text{S}=\text{CCF}_2\text{OSO}_2$  has opened a new pathway for preparing  $\text{SF}_6$  containing  $\beta$ -fluorosultones [7,19]:



In addition to liquid SO<sub>2</sub> [29], other solvents used with SO<sub>3</sub> in forming β-fluorosultones have been 1,1,2-trichloro-trifluoroethane (Freon 113) [16] and dimethyl sulfate [10].

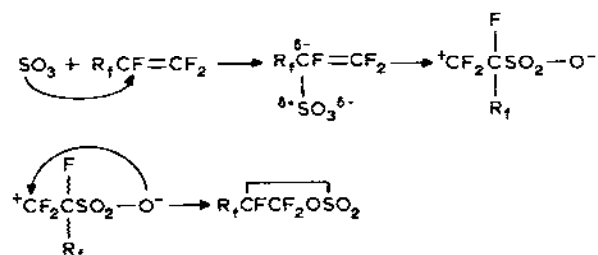
#### F. MECHANISMS FOR THE FORMATION OF THE $\beta$ -FLUOROSULTONES

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

(i) *Electrophilic mechanism*

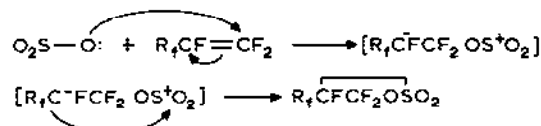
The reaction of sulfur trioxide and fluoro-olefins is proposed as an electrophilic reaction because of the electrophilic character of sulfur trioxide which easily adds to amines, ethers, alcohols, alkyl halides, hydrogen halides, water, and finally fluoro-olefins [10].

Sulfur trioxide reacts with fluoro-olefins through an unshared electron pair of the sulfur heteroatom and the  $\pi$  component of the multiple bond. The resulting intermediate  $\pi$  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  $\beta$ -sultones are formed [10,42].



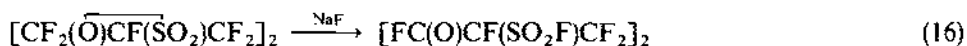
(ii) *Nucleophilic mechanism*

In this proposed scheme, a lone pair of electrons on an oxygen of sulfur trioxide attacks the carbon of the CF<sub>2</sub> 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]:





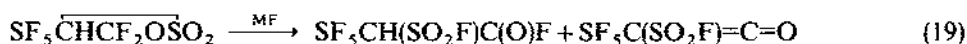
Bis-fluorosultones also undergo similar rearrangement [37,38]:



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



With an  $\text{SF}_5$ -sultone, not only rearrangement but dehydrofluorination was found [44]:



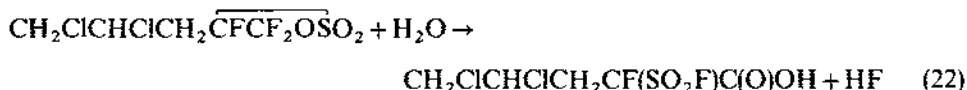
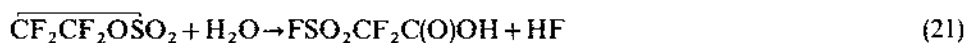
A second kind of isomerization has also been reported for  $\overline{\text{CF}_2\text{CF}_2}\overline{\text{OSO}_2}$  and occurs on storage at room temperature [1]:



In one report, it was found that  $\overline{\text{CF}_2\text{CF}_2}\overline{\text{OSO}_2}$  purified by gas chromatography upon standing at  $-78^\circ\text{C}$  for several days formed a chain-like polymer [1]; this material, however, is not stable.

## (ii) Hydrolysis reactions

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



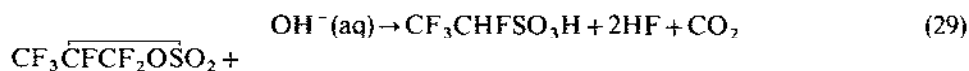
For all other  $\beta$ -fluorosultones, the resulting carboxylic acid is unstable and decomposes:



$\text{Z} = \text{SF}_5$ ,  $\text{X} = \text{F}$  [17]; and  $\text{SF}_5$ ,  $\text{H}$  [6]

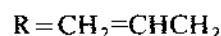
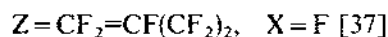
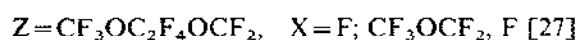
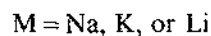
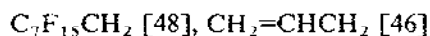
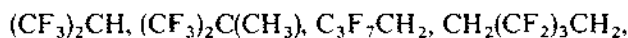
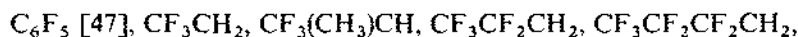
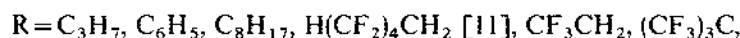
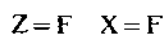
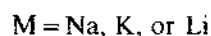
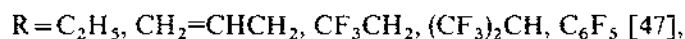
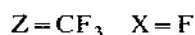
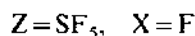
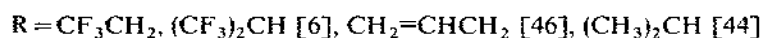
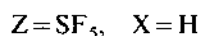
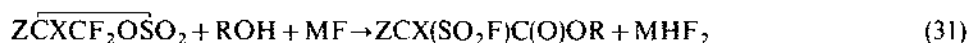
$\text{Z} = \text{CF}_3$ ,  $\text{X} = \text{F}$  [11];  $\text{CF}_3$ ,  $\text{H}$  [21];  $\text{CF}_2\text{ClCFClCF}_2$  and





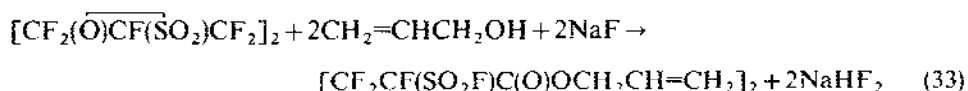
(iii) Reaction with alcohols/alkoxides

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



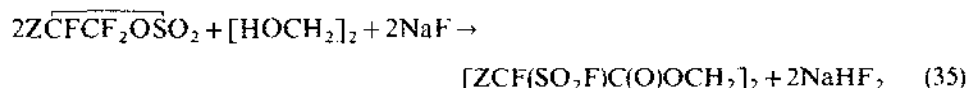
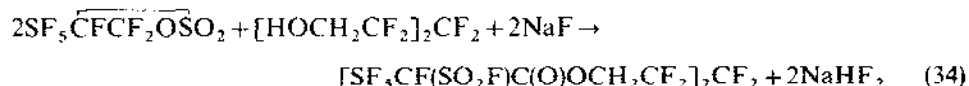
In a series of reactions with  $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$  and  $\text{CH}_2=\text{CHCH}_2\text{OH}$ , the polyester  $(\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CHCH}_2-)_n$  was produced. For a

bis  $\beta$ -fluorosultone, the corresponding bis ester is produced [37]:

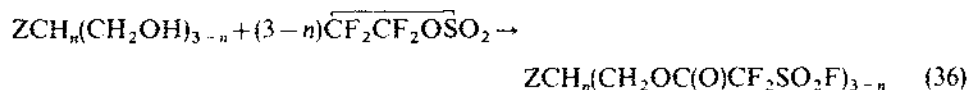


Polymerization of the diester gave  $[(-\text{CH}_2\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2)_2]_n$ , a solid polymer that is stable above  $250^\circ\text{C}$  [37].

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



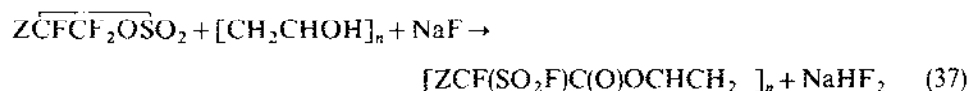
$\text{Z} = \text{F}, \quad \text{Z} = \text{CF}_3$



$\text{Z} = \text{CH}_3, \text{NO}_2, \text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}, \text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$

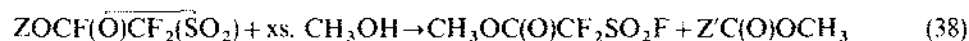
$n = 0, 1, 2, 3$  [48]

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



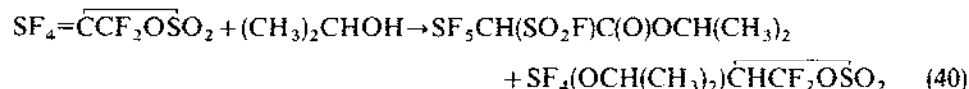
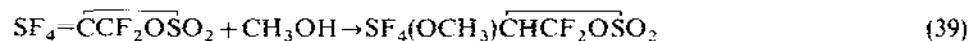
$\text{Z} = \text{F}$  and  $\text{CF}_3$ ;  $n \approx 318$ , soluble in acetone; decomposes at  $120^\circ\text{C}$ ,  $170^\circ\text{C}$ .

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



$\text{Z} = \text{C}_3\text{F}_7, \text{C}_4\text{F}_9$ ;  $\text{Z}' = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$

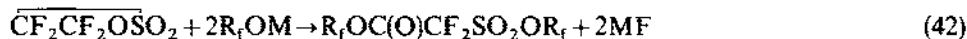
For the exocyclic sultone  $\text{F}_4\text{S}=\text{CCF}_2\text{OSO}_2$ , reaction with different alcohols has been studied. With  $\text{CH}_3\text{OH}$ , a new  $\beta$ -fluorosultone was isolated but attempts to isolate the  $\beta$ -fluorosultone,  $\text{SF}_4(\text{OCH}(\text{CH}_3)_2)\text{CHCF}_2\text{OSO}_2$ , in eqn. (40) failed; NMR studies confirmed its existence [7]:



With  $(\text{CH}_3)_3\text{COH}$ , only the resulting ester was found:



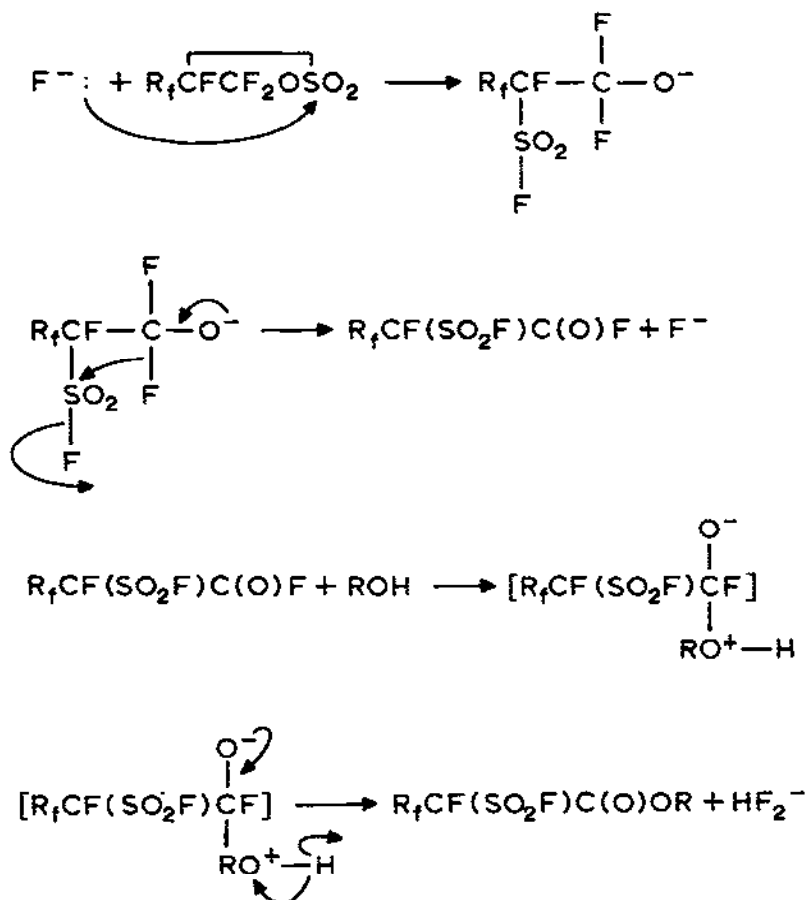
Another method for the formation of fluoroesters is the reaction between  $\beta$ -fluorosultones and alkoxides [11,48]:



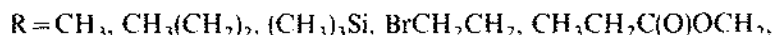
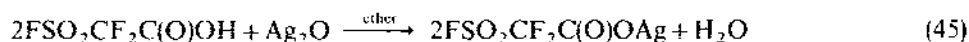
$\text{R}_f = \text{CF}_3\text{CH}_2$  and  $(\text{CF}_3)_2\text{CH}$ ,  $\text{M} = \text{Li}$



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



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

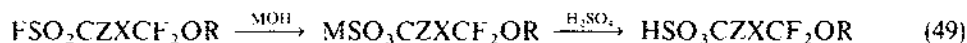


With  $\text{CH}_2\text{I}_2$  the corresponding diester,  $[\text{FSO}_2\text{CF}_2\text{C(O)O}]_2\text{CH}_2$ , was formed.

It should be noted that treatment of fluorocsters with  $\text{SF}_4/\text{HF}$  leads to the corresponding ethers [50]:

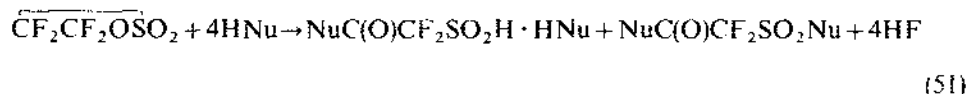
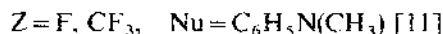
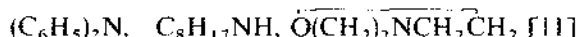
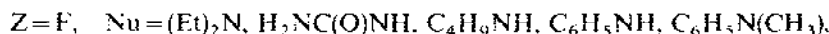


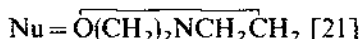
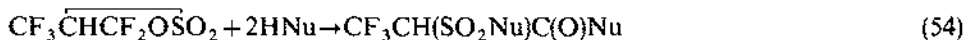
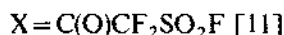
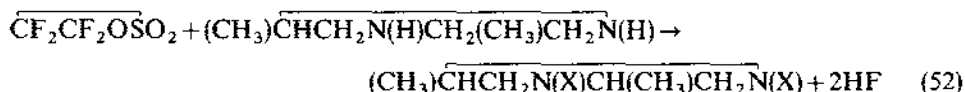
The ether product can be converted into its corresponding sulfonic acids. Thus we have a method, starting with  $\beta$ -fluorosultones and alcohols, that can produce a great variety of structurally modified sulfonic acids via the general pathway:



#### (iv) Reaction with amines

As expected,  $\beta$ -fluorosultones also react with a variety of amines.



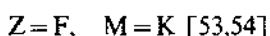
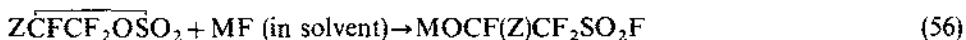


Reaction of  $\beta$ -fluorosultone with ammonia can lead to formation of diamides and amidoamidines [36]. Adding  $\text{NH}_3$  to  $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$  in diethyl ether at  $0^\circ\text{C}$  gave  $\text{FSO}_2\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{NH}_2$  and  $\text{NH}_4\text{F}$ . Treatment of this amide with  $\text{P}_4\text{O}_{10}$  and heat in vacuo gave the corresponding cyanide and triazine [51].

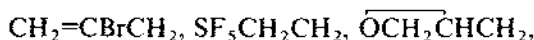
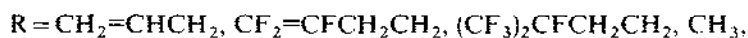
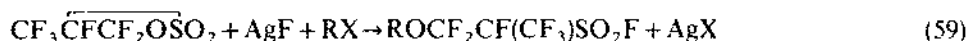
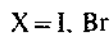
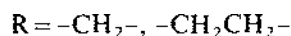
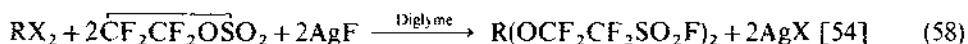
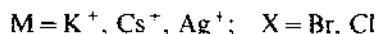
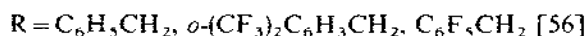
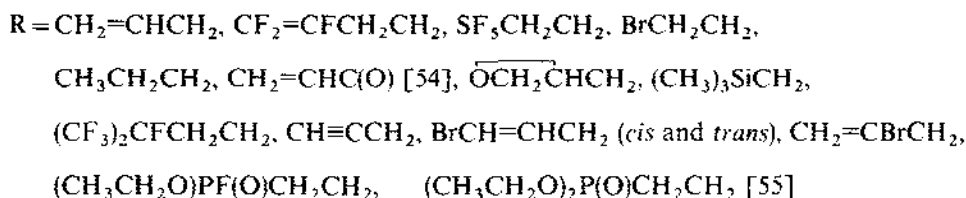
#### (v) Reaction with metal fluorides

The reaction of  $\beta$ -fluorosultones with metal fluorides has expanded their synthetic usefulness via formation of intermediate alkoxides. In one study,  $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{F}$  formed from  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$  was treated with a limited amount of  $\text{KF}$  in diglyme at  $40\text{--}50^\circ\text{C}$ ; the resulting fluoroalkoxides,  $\text{KOCF}_2\text{CF}_2\text{SO}_2\text{F}$ ,  $\text{KOCF}(\text{CF}_2\text{SO}_2\text{F})_2$  and  $\text{KOCF}(\text{CF}_2\text{SO}_2\text{F})\text{CF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ , which formed were treated with methyl fluorosulfate and their resulting methoxy derivatives  $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCH}_3$ ,  $\text{CH}_3\text{OCF}(\text{CF}_2\text{SO}_2\text{F})_2$ , and  $\text{CH}_3\text{OCF}(\text{CF}_2\text{SO}_2\text{F})\text{CF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$  were isolated [52].

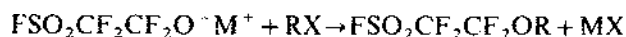
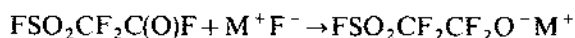
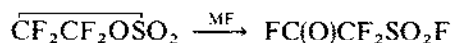
Additional fluoroalkoxides, either isolated or used as an intermediate, include  $\text{MOCF}_2\text{CF}_2\text{SO}_2\text{F}$  ( $\text{M} = \text{K}, \text{Cs}$ ),  $\text{MOCF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$  ( $\text{M} = \text{K}, \text{Cs}$ ) [53], and  $\text{AgOCF}_2\text{CF}_2\text{SO}_2\text{F}$  [54–58]; the isolated  $\text{MOCF}_2\text{CF}_2\text{SO}_2\text{F}$  ( $\text{M} = \text{K}, \text{Cs}$ ) compounds were found to be stable at room temperature but  $\text{MOCF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$  salts ( $\text{M} = \text{K}, \text{Cs}$ ) were unstable at room temperature.



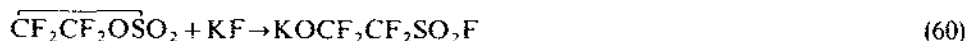
The alkoxides are useful intermediates for preparing a number of  $\text{FSO}_2$  precursors. The hypochlorites  $\text{ClOCF}_2\text{CFXSO}_2\text{F}$ , ( $\text{X} = \text{F}, \text{CF}_3$ ), were prepared using  $\text{ClF}$  or  $\text{ClSO}_3\text{F}$  and the corresponding alkoxides [53]. The sultones  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$  and  $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$  with  $\text{MF}$  ( $\text{M} = \text{K}, \text{Cs}$ , and  $\text{Ag}$ ) form the intermediate alkoxides that react with numerous alkyl halides [54–58]:



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 ≫ 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 <sup>-</sup>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F occurs. This mechanism is summarized as follows [54]:



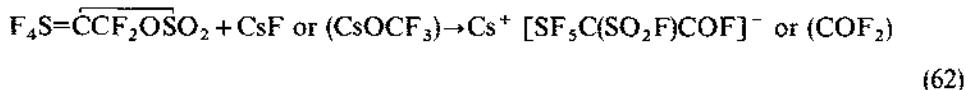
The β-fluorosultone  $\overline{CF_2CF_2OSO_2}$  can also be used to form the useful iodo derivative octafluoro-5-iodo-3-oxapentanesulfonyl fluoride, I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>F. It is prepared in a two-step reaction sequence [59]:



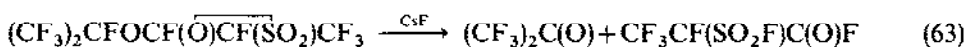


This material, in the presence of benzoyl peroxide, adds to a number of alkenes and alkynes [58,59] and is an important route for the preparation of a significant number of organic sulfonyl fluorides.

Some additional MF reactions of particular interest are: the exocyclic  $\beta$ -fluorosultone reaction with CsF or CsOCF<sub>3</sub> to give a very stable cesium salt [7,19]:



Treatment of  $(\text{CF}_3)_2\text{CFOCF}(\overline{\text{O}})\text{CF}(\text{SO}_2)\text{CF}_3$  with CsF results in the formation of the two compounds [32]:



(vi) Reaction with metal hydroxides

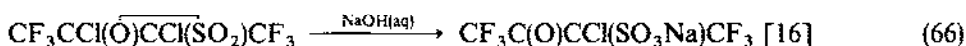
$\beta$ -Fluorosultones or their derivatives offer a convenient way to form fluorosulfonate salts from which the corresponding acids can be prepared.



Z = F [11], CFCF<sub>2</sub>CF<sub>2</sub>, CF<sub>2</sub>Cl(CFCF<sub>2</sub>)<sub>2</sub>, CF<sub>2</sub>Cl(CFCF<sub>2</sub>)<sub>3</sub>,

CF<sub>2</sub>Cl(CFCF<sub>2</sub>)<sub>4</sub> [16], CF<sub>3</sub>, C<sub>5</sub>F<sub>11</sub> [36]

M = Li, Na, K, Sr, Ba



X = F M = Ca, Na [17]

X = H 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  $\beta$ -fluorosultone have been prepared [6,9,11,17,60-64]:

HSO<sub>3</sub>CF<sub>2</sub>C(O)OH, HCF<sub>2</sub>SO<sub>3</sub>H, CF<sub>3</sub>CFHSO<sub>3</sub>H, SF<sub>5</sub>CH<sub>2</sub>SO<sub>3</sub>H,

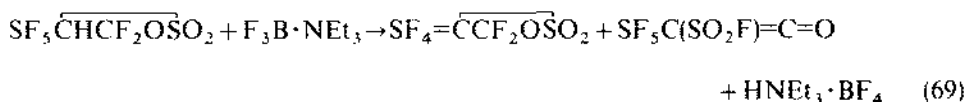
SF<sub>5</sub>CFHSO<sub>3</sub>H, SF<sub>5</sub>CF<sub>2</sub>SO<sub>3</sub>H, (HO)<sub>2</sub>P(O)CF<sub>2</sub>SO<sub>3</sub>H,

(HO)<sub>2</sub>P(O)CFHSO<sub>3</sub>H, (HO)<sub>2</sub>P(O)(CF<sub>2</sub>)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>H,

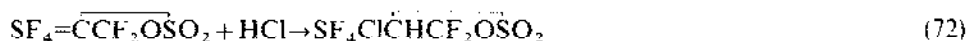
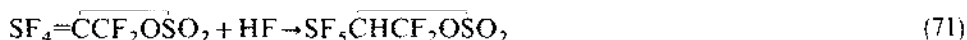
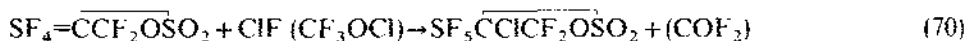
$R_f\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$  ( $R_f = \text{CF}_3\text{CH}_2$ ,  $\text{CF}_3\text{CF}_2\text{CH}_2$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2$ ),  
and  $\text{CFXYCF}_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$  ( $\text{XY} = \text{Cl}_2$ ,  $\text{HF}$ ,  $\text{FH}$ )

(vii) *Other reactions*

Dehydrohalogenation of appropriate  $\beta$ -fluorosultones is an effective way of generating unique  $\text{FSO}_2$ -containing ketenes [19,65]:

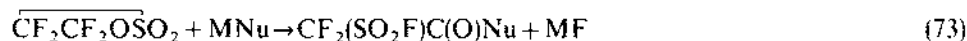


In addition to preparing the  $\text{SF}_5\text{C}(\text{SO}_2\text{F})=\text{C}=\text{O}$  ketene, the first cyclic example of a novel class of compounds, the alkylidenesulfur tetrafluoride,  $\text{SF}_4=\overline{\text{CCF}_2\text{OSO}_2}$ , was also prepared. This unique sultone holds promise for preparing additional  $\beta$ -fluoro-sultone derivatives [7,19]:



With  $\text{CH}_3\text{OH}$  and  $(\text{CH}_3)_2\text{CHOH}$ , the corresponding  $\beta$ -fluorosultones were produced [7]. Unfortunately, attempts at using fluoroalcohols failed [7]; with compounds such as  $\text{CsF}$  or  $\text{CsOCF}_3$ , the stable cesium salt,  $\text{Cs}^+[\text{SF}_5\text{C}(\text{SO}_2\text{F})\text{COF}]^-$  was formed (see eqn. (62)).

The HS and SCN derivatives of  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$  were prepared via the following pathways [11, 12]:



$\text{Nu} = \text{HS}, \text{SCN}; \quad \text{M} = \text{H}, \text{Na} \text{ (where Nu = SCN)}$

Mono- and polybasic aliphatic and aromatic acids react with  $\beta$ -fluorosultones to give mixed anhydrides which are effective acylating agents for alcohols, phenols, and thiols [1]. The reaction of  $\beta$ -fluorosultones with acyl chlorides produced derivatives of the fluoroalkenylsulfonic acid  $\text{RCF}=\text{CFOSO}_2\text{Cl}$ . For a more complete discussion that includes reaction of  $\beta$ -fluorosultones with alkyl chlorosulfates, sulfurous esters,  $(\text{RO})_2\text{SO}$ , alkanesulfonyl chlorides, and phosphorus and nitrogen oxychlorides, the reader is referred to the previous reviews [1,4].

H. SPECTRAL/STRUCTURAL PROPERTIES OF THE  $\beta$ -FLUOROSULTONES

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

$$r(\text{S}-\text{C})=1.77 \text{ \AA}; r(\text{C}-\text{F})=1.33 \text{ \AA}; r(\text{C}-\text{C})=1.45 \text{ \AA}$$

$$r(\text{C}-\text{O})=1.42 \text{ \AA}; r(\text{S}-\text{O})=1.60 \text{ \AA}; r(\text{S}-\text{O})=1.41 \text{ \AA}$$

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

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

In 1990, the X-ray crystal structure of the first  $\beta$ -fluorosultone,  $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ , was reported [8]; as is shown in Fig. 1, the  $\text{SF}_5$ -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  $\text{C}-\text{H}\cdots\text{O}$  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  $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$  has all hydrogen atoms and terminal oxygen atoms involved in intermolecular attractions. Only two of the  $\text{C}-\text{H}\cdots\text{O}$  distances are symmetry inequivalent, having values of 3.177 and 3.230 Å. While these distances are long

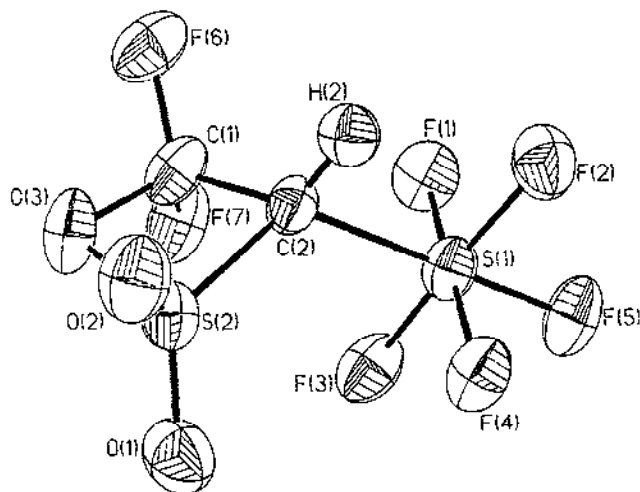


Fig. 1. Thermal ellipsoid view of  $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$  at 50% probability.

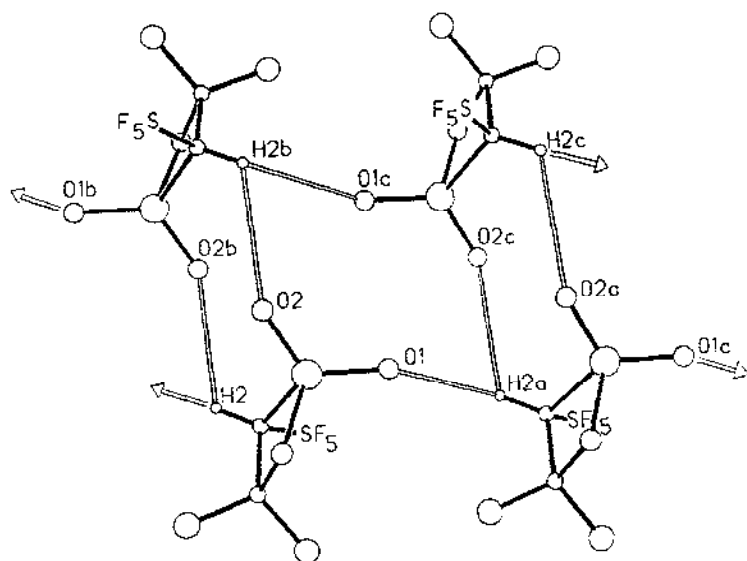


Fig. 2. Intermolecular hydrogen bonding in  $\text{SF}_5\text{CHCF}_2\text{OSO}_2$ .

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

The analyses of the  $^{13}\text{C}$  NMR spectra of some  $\beta$ -fluorosultones have recently been accomplished [6,7,19,34,68]. A complete listing of the chemical shifts along with respective coupling constants of  $\beta$ -fluorosultones are found below (see Table 5). If  $\text{CF}_2\text{CF}_2\text{OSO}_2$  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  $\alpha$  carbon. The strongest shieldings are found when H replaces F or when the  $\text{F}_4\text{S=}$  group replaces two F atoms; weaker shielding values for  $\text{CF}_3-$ ,  $\text{CF}_3\text{OCF}_2-$ , and  $\text{ClCH}_2\text{CHClCH}_2-$  were also found. The deshielding behavior shown by the  $\text{SF}_5$  and  $\text{SF}_4\text{Cl}$  groups suggest high electronegativity values for these groups; respective values in Pauling units of 3.62 and 3.48 were found. All  $\beta$  effects were reported to be very weak [68].

The  $^{13}\text{C}$ – $^{19}\text{F}$  coupling values vary within the range of  $\approx 270$ –330 Hz. These values are in good agreement with values reported for other cyclic system; for  $\text{c-C}_4\text{F}_8$  and  $\text{c-C}_4\text{F}_4\text{Cl}$ , the corresponding values are 298 and 300 Hz, respectively [69]. A large coupling constant ( $^1J_{\text{A}-\text{F}}$ ) increase is observed under the influence of electron withdrawal in going from  $\text{ClCH}_2\text{CHClCH}_2\text{CFCF}_2\text{OSO}_2$  or  $\text{CF}_3\text{CFCF}_2\text{OSO}_2$  to  $\text{CF}_2\text{CF}_2\text{OSO}_2$  or  $\text{SF}_5\text{CFCF}_2\text{OSO}_2$  [68].

The IR and NMR spectral data of many  $\beta$ -fluorosultones show relative comparable values, i.e. in the infrared spectra the  $\text{SO}_2$  asym stretch appears in the region  $1440$ – $1455\text{ cm}^{-1}$  while in the NMR spectra, the chemical shift of the  $\text{CF}_{2,1,2}(\text{O})$  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          |                      |
| <i>Ring bond lengths</i>     |                      |            |                      |
| SO                           | 1.669 Å              | 1.677(4) Å | 1.621(5) Å           |
| SC                           | 1.81 Å <sup>a</sup>  | 1.856(4) Å | 1.792(6) Å           |
| CO                           | 1.43 Å <sup>a</sup>  | 1.487(5) Å | 1.438(8) Å           |
| C-C                          | 1.581 Å <sup>a</sup> | 1.588(1) Å | 1.508(8) Å           |
| <i>Non-ring bond lengths</i> |                      |            |                      |
| C-H                          | 1.105 Å <sup>a</sup> | —          | 0.960 Å <sup>a</sup> |
| SO(1)                        | —                    | 1.466(4) Å | 1.408(5) Å           |
| SO(2)                        | —                    | —          | 1.401(4) Å           |
| <i>Ring bond angles</i>      |                      |            |                      |
| 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°<br>13.7°       |

<sup>a</sup> Assumed values.

TABLE 3  
Substitution effect on the <sup>13</sup>C NMR chemical shifts of  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$

| Sultone                                                            | X ( $\overline{\text{XCFCF}_2\text{OSO}_2}$ ) | Chemical shifts (ppm) |                 |
|--------------------------------------------------------------------|-----------------------------------------------|-----------------------|-----------------|
|                                                                    |                                               | XCF                   | CF <sub>2</sub> |
| $\text{CF}_3\overline{\text{CHCF}_2\text{OSO}_2}$                  | H                                             | ≈ -30                 | ≈ 0             |
| $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$                  | CF <sub>3</sub>                               | -13.5                 | -3.0            |
| $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$                  | H                                             | ≈ -30                 | ≈ 0             |
| $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$                  | SF <sub>5</sub>                               | +2.3                  | 0               |
| $\text{SF}_4\text{Cl}\overline{\text{CHCF}_2\text{OSO}_2}$         | SF <sub>4</sub> Cl                            | ≈ +13                 | ≈ 0             |
| $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$      | CF <sub>3</sub> OCF <sub>2</sub>              | -15.1                 | -1.2            |
| $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2\text{OSO}_2}$ | CH <sub>2</sub> ClCHClCH <sub>2</sub>         | -7.2                  | +0.3            |
| $\text{SF}_4=\overline{\text{CCF}_2\text{OSO}_2}$                  | =SF <sub>4</sub>                              | -45.3                 | +1              |

TABLE 4  
NMR data

| Sultone                                                               | Chemical shifts (ppm)                                                                            | Coupling constant (Hz) | Ref.     |
|-----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|------------------------|----------|
| $\overline{\text{CHFCF}}_{2(1,2)}\overline{\text{OSO}}_2$             | CF <sub>2</sub> (-83.9 d,d,d, -89.4 d,d,d)<br>CF (-170.2 d,d,d)<br>CH (6.4, d,d,d)               | $J_{1,2} = 111.5$      | 14       |
| $\overline{\text{CFClCF}}_{2(1,2)}\overline{\text{OSO}}_2$            | CF <sub>2</sub> (-83.9, -87.6)<br>CF (-103.0)                                                    | $J_{1,2} = 96.5$       | 15       |
| $\overline{\text{CF}}_{2(1,2)}\overline{\text{CFClOSO}}_2$            | CF <sub>2</sub> (-89.7, -74.5)<br>CF (-69.0)                                                     | $J_{1,2} = 119.3$      | 15       |
| $\overline{\text{CFBrCF}}_{2(1,2)}\overline{\text{OSO}}_2$            | CF <sub>2</sub> (-80.1, -87.4)<br>CF (-103.2)                                                    | $J_{1,2} = 95.6$       | 15       |
| $\overline{\text{CFICF}}_{2(1,2)}\overline{\text{OSO}}_2$             | CF <sub>2</sub> (-74.0, -88.2)<br>CF (-104.8)                                                    | $J_{1,2} = 95.5$       | 15       |
| $\text{FSF}_4\overline{\text{CFCF}}_{2(1,2)}\overline{\text{OSO}}_2$  | SF (62.7 m), SF <sub>4</sub> (57.0 m)<br>CF <sub>2</sub> (-81.2 d,p,d, -83.6 m)<br>CF (-116.9 m) | $J_{1,2} = 104.0$      | 17       |
| $\text{SF}_5\overline{\text{CHCF}}_{2(1,2)}\overline{\text{OSO}}_2$   | SF <sub>5</sub> (69.4 m)<br>CF <sub>2</sub> (-72.8 d, -79.7 d)<br>CH (6.58 m)                    | $J_{1,2} = 103.0$      | 6        |
| $\text{SF}_4\overline{\text{CCHCF}}_{2(1,2)}\overline{\text{OSO}}_2$  | SF <sub>4</sub> (67 m, 120 m, 141.7 m)<br>CF <sub>2</sub> (-74.9 d, -78.9 d,m)<br>CH (7.1 m)     | $J_{1,2} = 100.8$      | 19       |
| $\text{SF}_4\overline{\text{CCF}}_2\overline{\text{OSO}}_2$           | SF <sub>4</sub> (40.9, 47.2, 51.9)<br>CF <sub>2</sub> (-76.3)                                    | -                      | 19       |
| $\text{FSO}_3\overline{\text{CHCF}}_2\overline{\text{OSO}}_2$         | SO <sub>2</sub> F (68.1 m), CF <sub>2</sub> (-60.2 m)<br>CH (4.42 m)                             | -                      | 20       |
| $\overline{\text{CF}}_2\overline{\text{CF}}_2\overline{\text{OSO}}_2$ | CF <sub>2</sub> (-93.3 m, -102.6 m)                                                              | -                      | 11,14,53 |

|                                                                                              |                                                                                      |                                                                                                                            |                   |    |
|----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|-------------------|----|
| $\text{CF}_3\overline{\text{CHCF}}_{2(1,2)}\text{OSO}_2$                                     | $\text{CF}_3$<br>$\text{CH}$                                                         | (-64.5 m), $\text{CF}_2$ (-76.9 d,q)<br>(5.6 t,q)                                                                          | $J_{1,2} = 103.9$ | 21 |
| $\text{C}_2\text{H}_5\text{OC}(\text{CF}_3)\overline{\text{CF}}_{2(1,2)}\text{SO}_2\text{O}$ | $\text{CF}_3$<br>$\text{CF}_2$                                                       | (-77.6 d)<br>(-94.6 d, -100.5 d,q)                                                                                         | $J_{1,2} = 173$   | 26 |
| $\text{CF}_3\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                                     | $\text{CF}_2$<br>$\text{CF}_3$                                                       | (-82.4 m, -88.6 m)<br>(-74.4 d,t,m), $\text{CF}$ (-153.1 d,q)                                                              | $J_{1,2} = 107.2$ | 53 |
| $(\text{CF}_3)_2\overline{\text{CCF}}_2\text{OSO}_2$                                         | $\text{CF}_3$<br>$\text{CF}_2$                                                       | (-62.0)<br>(-76.3)                                                                                                         | -                 | 22 |
| $\text{HCF}_2\text{CF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                         | $\text{CF}_2(\text{O})$<br>$\text{CF}_2$<br>$\text{CF}$                              | (-82.7 m, -85.6 m)<br>(-122.2 m), $\text{HCF}_2$ (-137.9 m)<br>(-151.1 m), $\text{CH}$ (6.2 t,t)                           | $J_{1,2} = 100.1$ | 24 |
| $\text{CF}_2\text{ClCF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                        | $\text{CF}_2(\text{O})$<br>$\text{CF}_2\text{Cl}$<br>$\text{CF}$                     | (-81.6 m, -84.4 m)<br>(-86.3 m), $\text{CF}_2$ (-114.6 m)<br>(-149.3 m)                                                    | $J_{1,2} = 107.0$ | 24 |
| $\text{CF}_3\text{CF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                          | $\text{CF}_2$<br>$\text{CF}_3$<br>$\text{CF}$                                        | (-82.6 m, -85.9 m)<br>(-80.7 d,d), $\text{CF}_2$ (-121.0 m)<br>(151.3 m)                                                   | $J_{1,2} = 109.0$ | 24 |
| $\text{CF}_2\text{ClCFClCF}_2\overline{\text{CFCF}}_2\text{OSO}_2$                           | $\text{CF}_2\text{Cl}$<br>$\text{CF}_2$<br>$\text{CF}(\text{S})$                     | (-64), $\text{CF}_2(\text{O})$ (-83.0)<br>(-109), $\text{CFCl}$ (-128)<br>(-148)                                           | -                 | 31 |
| $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                    | $\text{CF}_2$<br>$\text{CF}$<br>$\text{CH}_2\text{Cl}$                               | (-82.3 d,d, -86.8 d,d)<br>(-145.3 d,m), $\text{CH}_2$ (3.6 m)<br>(4.2 m), $\text{CH}$ (4.8 m)                              | $J_{1,2} = 107.2$ | 34 |
| $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$                         | $\text{CF}_3$<br>$\text{CF}_2$<br>$\text{CF}$                                        | (-57.3 t), $\text{CF}_2\text{C}$ (-80.7 m)<br>(-85.4 d, d, t, -90.6 d, t)<br>(-153.9 d, t)                                 | $J_{1,2} = 112.9$ | 27 |
| $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$  | $\text{CF}_3$<br>$\text{CF}_2(\text{O})$<br>$\text{CF}_2\text{CF}$<br>$\text{OCF}_2$ | (-58.4 t)<br>(-85.3 d,d,t, -91.7 d,t)<br>(-79.5 m), $\text{CF}_2\text{O}$ (-90.9 m)<br>(-93.2 q), $\text{CF}$ (-154.7 d,t) | $J_{1,2} = 112.9$ | 27 |

TABLE 4 (continued)

| Sultone                                                                                                  | Chemical shifts (ppm)                                                                                                                                                                             | Coupling constant (Hz) | Ref. |
|----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|------|
| $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\text{O}\overline{\text{CF}}\text{CF}_{2(1,2)}\text{SO}_2\text{O}$ | $\text{CF}_3$ (-84.5 t)<br>$\text{CF}_2(\text{S})$ (-84.2 d,m, -87.0 d,m)<br>$\text{CF}_2\text{O}$ (-100.6 d,m, -102.8 d,m)<br>$\text{CF}$ (-91.8 m), $(\text{CF}_2)_2$ (-129.5 m)                | $J_{1,2} = 153.3$      | 30   |
| $(\text{CF}_3)_2\text{CFOCF}(\text{O})\overline{\text{CF}}(\text{SO}_2)\text{CF}_3$                      | $\text{CF}_3$ (-73.6 d,d), $(\text{CF}_3)_2$ (-80.5 m)<br>$\text{CF}(\text{O})$ (-83.7 m), $\text{CFO}$ (-143.1 d,m)<br>$\text{CF}(\text{S})$ (-149.6 d,q)                                        |                        | 32   |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\overline{\text{CF}}\text{CF}_{2(1,2)}\text{SO}_2\text{O}$     | $\text{CF}_3$ (-83.5 t)<br>$\text{CF}_2(\text{O})$ (-84.1 m, -86.5 m)<br>$\text{CF}_2\text{O}$ (-99.8 m, -101.2 m)<br>$\text{CF}$ (-90.3 m), $\text{CF}_2$ (-131.4 s)                             | $J_{1,2} = 151.0$      | 26   |
| $(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CF}}\text{CF}_{2(1,2)}\text{OSO}_2$                        | $\text{CF}_3$ (-81.3 m)<br>$\text{CF}_2(\text{O})$ (-82.4 d,d,t, -89.5 d,t)<br>$\text{OCF}_2$ (-74.6 m), $\text{CFO}$ (-145.7 t, sep)<br>$\text{CF}$ (-151.8 t,d)                                 | $J_{1,2} = 108.0$      | 33   |
| $(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CF}}\text{CF}_{2(1,2)}\text{OSO}_2$                        | $\text{CF}_3$ (-80.6 br,s)<br>$\text{CF}_2(\text{O})$ (-83.3 d,d,t, -89.0 d,t)<br>$\text{OCF}_2$ (-73.9 m), $\text{CFO}$ (-144.4 t,m)<br>$\text{CF}$ (-151.3 d,t)                                 | $J_{1,2} = 109.0$      | 32   |
| $(\text{CF}_3)_2\text{CFOCF}(\text{O})\overline{\text{CF}}(\text{SO}_3)\text{CF}_2\text{OSO}_2\text{F}$  | $\text{SO}_2\text{F}$ (51.2 m)<br>$\text{CF}_2$ (-77.1, AB center), $\text{CF}(\text{O})$ (-77.6 m)<br>$\text{CF}_3$ (-80.9 m), $\text{CF}$ (-145.2 d, sep)<br>$\text{CF}(\text{S})$ (-149.0 t,d) | —                      | 33   |
| $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\overline{\text{CF}}\text{CF}_{2(1,2)}\text{OSO}_2$                | $\text{CF}_3$ (-81.2 t,t)<br>$\text{CF}_2(\text{O})$ (-82.6 m, -85.5 m)<br>$(\text{CF}_2)_2$ (-116.7 m, -126.2 m)<br>$\text{CF}_2$ (-120.2 m), $\text{CF}$ (-151.2 m)                             | $J_{1,2} = 104.9$      | 24   |

|                                                                                           |                                                                                                    |                                                                                                                                |                   |    |
|-------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------------|----|
| $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$        | $\text{CF}_3$<br>$\text{CF}_2(\text{O})$<br>$(\text{CF}_2)_2$<br>$\text{CF}_2$                     | (-81.4 m)<br>(-82.4 d,m, -86.4 d,m)<br>(-119.7 m, -116.6 m)<br>(-125.6 m), CF (-151.2 m)                                       | -                 | 35 |
| $\text{C}_6\text{F}_5\text{CF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$              | $\text{CF}_2\text{O}$<br>$\text{CF}_2$<br>$\text{CF}$<br>$\text{C}_6\text{F}_5$                    | (-80.8 d,m, -87.6 d,m)<br>(-94.0 m, -97.2 m)<br>(-136.6 m)<br>(-137.5 m, -145.4 m, -163.5 m)                                   | $J_{1,2} = 109$   | 35 |
| $\text{F}_2\text{C}=\text{CFCF}_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$             | $\text{CF}_2(\text{O})$<br>$\text{CF}_2=$<br>$\text{CF}_2$<br>$=(\text{CF})$                       | (-81.4 m, AB center)<br>(-88.7 d,d,t, -105.1 d,t,t)<br>(-114.3 m), CF (-147.1 d,d,t)<br>(190.6 d,d,t)                          | -                 | 29 |
| $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$         | $\text{CF}_2$<br>$\text{CF}_2=$<br>$(\text{CF}_2)_2$<br>$\text{CF}$                                | (-84.5 d,t, -87.7 d,d,t)<br>(-89.3 d,d,t, -106.5 d,d,t,t)<br>(-119.9 d,d,m, -118.0 m)<br>(-152.9 m), CF= (-192.8 d,d,m)        | $J_{1,2} = 110.1$ | 37 |
| $[\text{CF}_2\text{CF}(\text{SO}_2)\text{CF}_{2(1,2)}(\text{O})]_2$                       | $\text{CF}_2(\text{O})$<br>$\text{CF}_2$                                                           | (-84.0 d,t, -86.7 d,m)<br>(-116.3 d,m), CF (-153.4 m)                                                                          | $J_{1,2} = 110.8$ | 37 |
| $\text{F}_2\text{C}=\text{CF}(\text{CF}_2)_4\overline{\text{CFCF}}_{2(1,2)}\text{OSO}_2$  | $\text{CF}_2(\text{O})$<br>$\text{CF}_2=$<br>$(\text{CF}_2)_4$<br>$(\text{CF}_2)_4$<br>$\text{CF}$ | (-83.6 m, AB center)<br>(-87.9 d,d,t, 105.1 d,d,t)<br>(-115.9 m -117.4 m)<br>(-119.0 m -122.6 m)<br>(-149.9 m), =CF (-189.7 m) | $J_{1,2} = 108.0$ | 38 |
| $[\text{CF}_{2(1,2)}(\text{O})\overline{\text{CF}(\text{SO}_2)\text{CF}_2\text{CF}_2}]_2$ | $\text{CF}_2(\text{O})$<br>$(\text{CF}_2)_2$<br>$\text{CF}$                                        | (-83.2 m, AB center)<br>(-115.5 m, -118.4 m)<br>(-150.2 m)                                                                     | $J_{1,2} = 107.2$ | 38 |

TABLE 5  
 $^{13}\text{C}$  NMR data

| Sultone                                                                                      | Chemical shifts (ppm)                                                                                                               | Coupling constant (Hz) | Ref. |
|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------------------|------|
| $\text{FSF}_4\overline{\text{CHC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                         | CH<br>CF <sub>2</sub><br>(99.6 d,p,m)<br>(112 br,p)                                                                                 | $J_{1,2} = 293.0$      | 6    |
| $\text{SF}_4\text{Cl}\overline{\text{CHC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                 | CF <sub>2</sub><br>CH<br>(113.4 t)<br>(108.8 d,m)                                                                                   | $J_{1,2} = 294.0$      | 19   |
| $\text{SF}_4=\overline{\text{CC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                          | =C<br>CF <sub>2</sub><br>(80.7 ≈ p,t)<br>(114.5 d,t)                                                                                | $J_{1,2} = 282.4$      | 19   |
| $\overline{\text{CF}}_2\text{C}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                            | CF <sub>2</sub><br>CF <sub>2</sub> O<br>(126.0 t,t)<br>(113.5 t,t)                                                                  | $J_{1,2} = 294.3$      | 68   |
| $\text{CF}_3\overline{\text{CFC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                          | CF <sub>3</sub><br>CF<br>CF <sub>2</sub><br>(117.2 q,d,m)<br>(112.5 d,m)<br>(110.5 t,d)                                             | $J_{1,2} = 293.6$      | 68   |
| $\text{CF}_3\overline{\text{CHC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                          | CF <sub>3</sub><br>CH<br>CF <sub>2</sub><br>(118.4 q)<br>(79.3 q,d,d)<br>(111.2 t,q)                                                | $J_{1,2} = 291.0$      | 68   |
| $\text{FSF}_4\overline{\text{CFC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$                         | CF<br>CF <sub>2</sub><br>(128.3 d,m)<br>(113.5 t,p)                                                                                 | $J_{1,2} = 298.0$      | 68   |
| $\text{CF}_3\text{OCF}_2\overline{\text{CFC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$              | CF <sub>3</sub><br>OCF <sub>2</sub><br>CF <sub>2</sub><br>CF<br>(119.2 q,m)<br>(114.7 m)<br>(112.3 d,d,m)<br>(110.9 d,m)            | $J_{1,2} = 294.0$      | 68   |
| $\text{C}'\text{H}_2\text{ClCHClCH}_2\overline{\text{CFC}}_{(2)}\text{F}_{2(1)}\text{OSO}_2$ | CF <sub>2</sub><br>CF<br>CH <sub>2</sub><br>C'H <sub>2</sub><br>(113.8 d,d,d)<br>(118.9 d,d,d)<br>(32.4 d), CH (51.7 s)<br>(46.8 s) | $J_{1,2} = 290.0$      | 34   |

TABLE 6  
MS data

| Sultone                                                                                    | Fragment ions ( <i>m/e</i> )                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Ref. |
|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$                                          | 208 (M-SO <sub>3</sub> ) <sup>+</sup> , 161 (M-SF <sub>5</sub> ) <sup>+</sup> ,<br>129 (CF(SO)CF <sub>2</sub> ) <sup>+</sup> , 127 (SF <sub>5</sub> ) <sup>+</sup> ,<br>113 (CF(S)CF <sub>2</sub> ) <sup>+</sup> , 97 (CFCF <sub>2</sub> O) <sup>+</sup> ,<br>81 (CFCF <sub>2</sub> ) <sup>+</sup> , 80 (SO <sub>3</sub> ) <sup>+</sup> , 66<br>(CF <sub>2</sub> O) <sup>+</sup> , 64 (SO <sub>2</sub> ) <sup>+</sup> , 51 (SF) <sup>+</sup> ,<br>48 (SO) <sup>+</sup>                                                                                               | 17   |
| $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$                                          | 269 (M-H) <sup>-</sup> , 142 (CCF <sub>2</sub> OSO <sub>2</sub> ) <sup>-</sup> ,<br>127 (SF <sub>5</sub> ) <sup>-</sup> , 123 (CCFSO <sub>3</sub> ) <sup>-</sup> ,<br>83 (SF <sub>2</sub> CH) <sup>-</sup> , 79 (CHCF <sub>2</sub> O) <sup>-</sup>                                                                                                                                                                                                                                                                                                                   | 6    |
| $\text{SF}_4=\overline{\text{CCF}_2\text{OSO}_2}$                                          | 250 (M) <sup>-</sup> , 170 (M-SO <sub>3</sub> ) <sup>+</sup> ,<br>165 (SF <sub>3</sub> CSO <sub>2</sub> ) <sup>+</sup> , 151 (M-SO <sub>3</sub> F) <sup>+</sup> ,<br>94 (C <sub>2</sub> F <sub>2</sub> S) <sup>+</sup> , 89 (SF <sub>3</sub> ) <sup>+</sup> , 70 (SF <sub>2</sub> ) <sup>+</sup> ,<br>64 (SO <sub>2</sub> ) <sup>-</sup> , 51 (SF) <sup>+</sup>                                                                                                                                                                                                      | 7    |
| $\text{SF}_4\overline{\text{ClCHCF}_2\text{OSO}_2}$                                        | 269 (M-O) <sup>-</sup> , 167 (M-HCl, SO <sub>2</sub> F) <sup>-</sup> ,<br>142 (M-HCl, SF <sub>4</sub> ) <sup>-</sup> , 120 (SF <sub>4</sub> C) <sup>-</sup> ,<br>108 (SF <sub>4</sub> ) <sup>-</sup> , 101 (CSF <sub>3</sub> ) <sup>-</sup> ,<br>89 (SF <sub>3</sub> ) <sup>-</sup> , 70 (SF <sub>2</sub> ) <sup>-</sup>                                                                                                                                                                                                                                             | 7    |
| $\text{C}^{37}\text{Cl}\overline{\text{ClCHClCH}_2\text{CFCF}_2\text{OSO}_2}$              | 239 (M- <sup>37</sup> Cl) <sup>+</sup> , 237 (M- <sup>35</sup> Cl) <sup>+</sup> ,<br>161 (CF(SO <sub>2</sub> )CF <sub>2</sub> (O)) <sup>+</sup> ,<br>142 (CF <sub>2</sub> CSO <sub>3</sub> ) <sup>+</sup> , 108 (CF <sub>2</sub> CFC <sub>2</sub> H <sub>3</sub> ) <sup>+</sup> ,<br>95 (CFSO <sub>2</sub> ) <sup>-</sup> , 80 (SO <sub>3</sub> ) <sup>-</sup> ,<br>64 (SO <sub>2</sub> ) <sup>+</sup> , 62 (CCF <sub>2</sub> ) <sup>+</sup>                                                                                                                         | 34   |
| $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$                              | 297 (MH) <sup>+</sup> , 277 (MH-HF) <sup>+</sup> ,<br>216 (M-SO <sub>3</sub> ) <sup>-</sup> , 211 (M-CF <sub>3</sub> O) <sup>+</sup> ,<br>179 (CF <sub>3</sub> OCF <sub>2</sub> CS) <sup>+</sup> , 145 (CF(SO <sub>2</sub> )CF <sub>2</sub> ) <sup>+</sup> ,<br>128 (CF <sub>2</sub> OCFC) <sup>-</sup> , 95 (CFSO <sub>3</sub> ) <sup>+</sup> ,<br>80 (SO <sub>3</sub> ) <sup>+</sup> , 69 (CF <sub>3</sub> ) <sup>+</sup> , 64 (SO <sub>2</sub> ) <sup>+</sup>                                                                                                     | 27   |
| $\text{CF}_3\text{O}(\text{CF}_2)_2\text{OCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$       | 413 (MH) <sup>-</sup> , 393 (M-F) <sup>+</sup> ,<br>332 (M-SO <sub>3</sub> ) <sup>+</sup> , 327 (M-CF <sub>3</sub> O) <sup>+</sup> ,<br>185 (CF <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> ) <sup>+</sup> , 163 (CF <sub>3</sub> OCFCFO) <sup>-</sup> ,<br>135 (CF <sub>3</sub> OCF <sub>2</sub> ) <sup>+</sup> , 129 (CF(SO)CF <sub>2</sub> ) <sup>+</sup> ,<br>100 (CF <sub>2</sub> CF <sub>2</sub> ) <sup>+</sup> , 95 (CFSO <sub>2</sub> ) <sup>+</sup> ,<br>79 (CFSO) <sup>+</sup> , 69 (CF <sub>3</sub> ) <sup>-</sup> , 64 (SO <sub>2</sub> ) <sup>-</sup> | 27   |
| $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\text{O}\overline{\text{CFCF}_2\text{SO}_2\text{O}}$ | 397 (MH) <sup>+</sup> , 316 (M-SO <sub>3</sub> ) <sup>+</sup> ,<br>263 (M-CF <sub>2</sub> SO <sub>2</sub> F) <sup>+</sup> , 225 (C <sub>4</sub> F <sub>7</sub> OCO) <sup>+</sup> ,<br>219 (C <sub>4</sub> F <sub>9</sub> ) <sup>+</sup> , 177 (OCF(O)CF <sub>2</sub> SO <sub>2</sub> ) <sup>+</sup> ,<br>169 (C <sub>3</sub> F <sub>7</sub> ) <sup>+</sup> , 113 (CFCF <sub>2</sub> S) <sup>+</sup> ,<br>78 (CF <sub>2</sub> CO) <sup>-</sup> , 69 (CF <sub>3</sub> ) <sup>+</sup> ,<br>64 (SO <sub>2</sub> ) <sup>+</sup> , 63 (CFS) <sup>+</sup>                   | 30   |

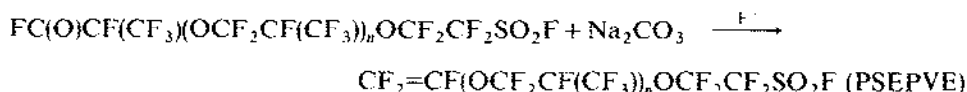
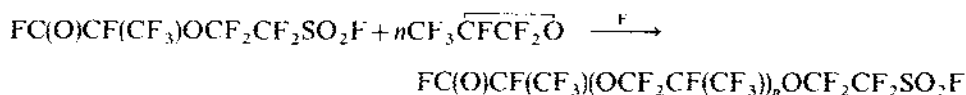
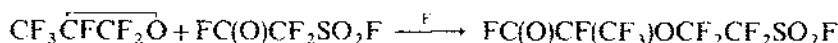
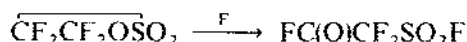
TABLE 6 (continued)

| Sultone                                                                    | Fragment ions ( <i>m/e</i> )                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Ref. |
|----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$ | 342 ( $\text{M}$ ) <sup>+</sup> , 323 ( $\text{M}-\text{F}$ ) <sup>+</sup> , 231 ( $\text{C}_5\text{F}_9$ ) <sup>+</sup> ,<br>212 ( $\text{C}_5\text{F}_8$ ) <sup>+</sup> , 193 ( $\text{M}-\text{CF}_3\text{SO}_3$ ) <sup>+</sup> ,<br>155 ( $\text{C}_5\text{F}_5$ ) <sup>+</sup> , 109 ( $\text{C}_3\text{F}_3\text{O}$ ) <sup>+</sup> ,<br>95 ( $\text{CF}_3\text{SO}_2$ ) <sup>+</sup> , 79 ( $\text{CF}_3\text{SO}$ ) <sup>+</sup> , 64 ( $\text{SO}_2$ ) <sup>+</sup> ,<br>48 ( $\text{SO}$ ) <sup>+</sup> , 47 ( $\text{CFO}$ ) <sup>+</sup> , 44 ( $\text{CS}$ ) <sup>+</sup>                                                                                      | 37   |
| $[\text{CF}_2(\overline{\text{O}})\text{CF}(\text{SO}_2)\text{CF}_2]_2$    | 423 ( $\text{MH}$ ) <sup>+</sup> , 403 ( $\text{M}-\text{F}$ ) <sup>+</sup> ,<br>342 ( $\text{M}-\text{SO}_3$ ) <sup>+</sup> , 259 ( $\text{C}_6\text{F}_9\text{O}$ ) <sup>+</sup> ,<br>231 ( $\text{C}_6\text{F}_5\text{SO}_2$ ) <sup>+</sup> , 181 ( $\text{C}_4\text{F}_7$ ) <sup>+</sup> ,<br>169 ( $\text{C}_4\text{F}_3\text{SO}_2$ ) <sup>+</sup> , 143 ( $\text{C}_4\text{F}_5$ ) <sup>+</sup> ,<br>95 ( $\text{CF}_3\text{SO}_2$ ) <sup>+</sup> , 81 ( $\text{C}_2\text{F}_4$ ) <sup>+</sup> ,<br>79 ( $\text{CF}_3\text{SO}$ ) <sup>+</sup> , 66 ( $\text{CF}_2\text{O}$ ) <sup>+</sup> ,<br>64 ( $\text{SO}_2$ ) <sup>+</sup> , 63 ( $\text{CFS}$ ) <sup>+</sup> | 37   |

values of 100–110 Hz. Knowledge of these spectral characteristics is necessary in order to determine the structures of new  $\beta$ -sultones. A complete listing of known spectral values including IR, NMR, and MS data are given in Tables 1 and 4–6. The  $^{19}\text{F}$  NMR chemical shifts of the  $\beta$ -sultones are reported relative to F-11 ( $\text{CFCl}_3$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  NMR relative to TMS ( $(\text{CH}_3)_4\text{Si}$ ).

#### 1. USES OF THE $\beta$ -FLUOROSULTONES

One of the principal uses found for  $\beta$ -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  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$  via the following sequence [70,71]:



The polymeric material (PSEPVE) is copolymerized with  $\text{CF}_2=\text{CF}_2$  to form a poly-

meric 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  $\beta$ -fluorosultones:  $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ ,  $\overline{\text{CF}_3\text{CFCF}_2\text{OSO}_2}$ ,  $\overline{\text{SF}_5\text{CFCF}_2\text{OSO}_2}$ , and  $\overline{\text{SF}_5\text{CHCF}_2\text{OSO}_2}$  with polyvinyl and allyl alcohols [46].

A number of fluorocarbon vinyl sulfonyl fluorides of the type  $\text{CF}_2=\text{CF}(\text{CFR})_n\text{CFHSO}_2\text{F}$  where  $\text{R}=\text{F}$  or perfluoroalkyl group and  $n=1-5$  or of the type  $\text{ROCF}_2\text{CFXSO}_2\text{F}$  where  $\text{X}=\text{F}$ ,  $\text{CF}_3$  and  $\text{R}=\overline{\text{OCH}_2\text{CHCH}_2}$ ,  $\text{HC}\equiv\text{CCH}_2$ ,  $\text{H}_2\text{C}=\text{CHCH}_2$ ,  $\text{F}_2\text{C}=\text{CF}(\text{CH}_2)_2$  have been reported [31,54,55,57]. These materials should be useful comonomers with other fluoro-olefins such as  $\text{CF}_2=\text{CF}_2$  in the preparation of polymers with ion-exchange capabilities.

Copolymerization of  $\text{CF}_2=\text{CFSO}_2\text{F}$  (formed from  $\overline{\text{CF}_3\text{CFCF}_2\text{OSO}_2}$ ) 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  $\beta$ -fluorosultones and it is expected that, in this area, extensive use of  $\beta$ -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.  $(\text{HO})_2\text{P}(\text{O})\text{CF}_2\text{SO}_3\text{H}$  and  $\text{SF}_5\text{CF}_2\text{SO}_3\text{H}$  [61,63,64]. The  $\text{SF}_5\text{CF}_2\text{SO}_3\text{H}$  acid is an analogue to triflic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ).

Biological activity has also been reported for a number of derivatives prepared from  $\beta$ -fluorosultones [75]. Another proposed use of  $\beta$ -fluorosultones is as a stabilizer for liquid  $\text{SO}_3$  [76].

The ability of the  $\beta$ -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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