#### ORGANIC AND BIOLOGICAL CHEMISTRY

# FLUORINE-CONTAINING $\beta$ -SULTONES

## COMMUNICATION 15. ALKYL FLUOROSULFATES

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We have previously reported [1] that the main products of the reaction of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone with chlorosulfuric acid are trifluorovinyl chlorosulfate and fluorosulfuric acid:

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This course of the process is determined, on the one hand, by the ability of fluorine-containing  $\beta$ -sultones to undergo anionotropic transformations because of the high mobility of the fluorine on the  $\beta$ -carbon atom and, on the other, by the electron-acceptor character of the sulfonyl group in the chlorosulfuric acid molecule. It may be supposed that, if instead of chlorosulfuric acid we use other compounds containing the chlorosulfonyl group, these will react with tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone by an analogous mechanism. To check this supposition we have studied the behavior of various chlorosulfonyl-containing compounds toward tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone.

It was shown that conditions can be found under which tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone will react with methanesulfonyl chloride, alkyl chlorosulfates, and sulfuryl chloride. In all cases one of the reaction products was trifluorovinyl chlorosulfate; the other products isolated were, respectively, methanesulfonyl fluoride, alkyl fluorosulfates, and sulfuryl chloride fluoride. The reaction conditions and the yields of the trifluorovinyl chlorosulfate formed are given in Table 1; for comparison we also give the results of the reaction of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone with chlorosulfuric acid [1].

It will be seen from Table 1 that the temperature conditions for reaction and the yield of trifluorovinyl chlorosulfate are determined by the nature of the substituent attached to the chlorosulfonyl group in the substance reacting with the sultone. The conditions for reaction are most favorable when the compound used is methanesulfonyl chloride, i.e., a compound whose chlorosulfonyl chlorine is highly mobile because of the considerable positive induction effect of the methyl substituent. As the electron-accepting power of the substituent is increased along the series  $CH_3$ , RO, HO, Cl, the mobility of chlorine in the molecule of the reactant diminishes and the reluctance to react increases. Thus, in the case of sulfuryl chloride, for which reactions of the radical type are the most characteristic, reaction with tetrafluoro-2hydroxyethanesulfonic  $\beta$ -sultone can be brought about only at high temperature (100° or higher). The low yield of trifluorovinyl chlorosulfate arises from the isomerization of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone under the conditions of the reaction [2]: it is converted into difluoro(fluorosulfonyl)acetyl fluoride, which is inert toward sulfuryl chloride. In the reaction mixture we actually found difluoro(fluorosulfonyl)acetyl fluoride (62.5%) and unchanged sulfuryl chloride (70%); the conversion of the sultone was more than 80%.

Hence, the reactions of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone with chlorosulfonyl-containing compounds proceed in accordance with a common pattern and may be described by the scheme:



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TABLE 1

XSO <sub>2</sub> Cl taken	Reaction temp., °C	Yield of ClSO <sub>2</sub> OC F = C F <sub>2</sub> , %	XSO <sub>2</sub> F obtained
$\begin{array}{c} CH_3SO_2C1\\ ROSO_2C1\\ HOSO_2C1\\ C1SO_2C1\\ \end{array}$	20	95	$CH_3SO_2F$
	30-60	75-80	$ROSO_2F$
	80	70	$HOSO_2F$
	100	20	$C1SO_2F$

TABLE 2

	Bp ℃	20	-	MR			
Compound	(p, mm)	$d_4^{20}$	$n_{D}^{20}$	fo <b>un</b> d	calculated		
$\rm CH_3OSO_2F$	91-92	1,4256	1.3440	16.94	17.15		
$C_2H_5OSO_2F$	112-113	1.2678	1.3512	21.81	21.80		
n-C <sub>3</sub> H <sub>7</sub> OSO <sub>2</sub> F	49 (35)	1.1890	1.3612	26.45	26.46		
n-C <sub>4</sub> H <sub>9</sub> OSO <sub>2</sub> F	59 (35)	1.1362	1.3720	31.24	31.08		
$n-C_5H_{11}OSO_2F$	63 (25)	1.1140	1.3840	35.72	35.75		
$n-C_6H_{13}OSO_2F$	60 (2)	1,0932	1,3952	40.42	40,35		

Since the reaction takes this course, it can be regarded as providing a general method for the preparation of alkyl fluorosulfates. Before the present work no general method was known for the preparation of unsubstituted alkyl fluorosulfates; only two compounds of this type have been described in the literature — methyl and ethyl fluorosulfates [3].

This method for the preparation of alkyl fluorosulfates was tested out for the case of the reactions of tetrafluoro-2-hydroxyethylsulfonic  $\beta$ -sultone with methyl, ethyl, propyl, butyl, pentyl, and hexyl chlorosulfates. In all cases, as well as trifluorovinyl chlorosulfate, we isolated the corresponding alkyl fluorosulfates, the physical properties of which are given in Table 2.

Molecular refractions were calculated with the use of the average value of the refraction of the fluorosulfate group  $R_{OSO_2F} = 11.50$ , as deduced from the experimental values of densities and refractive indices of alkyl fluorosulfates. An interesting conclusion may be drawn from a comparison of the refractions of halosulfate (halosulfonyloxy) and halosulfonyl groups. It was found that the change in the refraction as we pass from the fluorine- to the chlorine-containing group is almost the same in the alkyl halosulfate and alkanesulfonyl halide series:

It may be supposed that a similar change in the refraction will be observed as we pass from fluoride to chloride in the case of other types of acid halide. Thus, if the atomic refraction of chlorine in carboxylic acid chlorides is 6.336 [4], then the value for fluorine would be expected to be about 1.47, which differs considerably from the accepted values of  $R_f = 0.997-1.35$  [4].

The chemical properties of alkyl fluorosulfates which we studied were their behavior toward water, toward sodium chloride, and toward triethylamine. In all cases alkyl fluorosulfates behave as extremely effective alkylating agents. Thus, they react vigorously with water with formation of fluorosulfuric acid and an alcohol. This is the only course of reaction even in the treatment of alkyl fluorosulfates with aqueous solutions of alkalies:

$$ROSO_2F + NaOH \rightarrow ROH + NaOSO_2F.$$

When sodium chloride is treated with alkyl fluorosulfates, the corresponding alkyl chlorides can be isolated in good yields:

$$ROSO_2F + NaCl \rightarrow RCl + NaOSO_2F.$$

TABLE 3													
	Reaction con	nditions	Yield of	ROSO <sub>2</sub> F obtained			Fou	nd %			Calcul	ated %	
ROSO <sub>2</sub> CI Laken	temp., °C	time, h	CLSO2OCF=CF2	formula	yield, %	С	Н	Ч	ß	C	Н	Ľ٩	w
CH <sub>3</sub> OSO <sub>2</sub> CI	50-60	4	75	$ m CH_3OSO_2F$	70	I	I	16.81	28.06	3	ŀ	16.67	28.03
$C_2H_5OSO_2CI$	50-60	4	75	$\rm C_2H_5OSO_2F$	75	1	I	15.18	25.12	ı	i	14.84	25.00
$n-C_3H_7OSO_2CI$	40-50	2-3	77	$\mathrm{n-C_3H_7OSO_2F}$	65	25.15	4.81	13.70	22.30	25.37	4.93	13.40	22.51
$n-C_4H_9OSO_2CI$	40-50	2-3	78	$n-C_4H_9OSO_2F$	60	30.58	5.50	12.42	20.45	30.76	5.77	12.18	20.50
$n-C_5H_{11}OSO_2CI$	30-40	1	80	$n-C_5H_{11}OSO_2F$	68	35.10	6.30	11.40	18.86	35.28	6.48	11.16	18,82
$n-C_6H_{13}OSO_2CI$	30-40		80	$n-C_6H_{13}OSO_2F$	76	38.92	6.82	10.48	17.60	39.06	7.06	10.32	17.39

The reactions of alkyl fluorosulfates with triethylamine take place even at  $-20^{\circ}$  with quantitative formation of the corresponding quaternary ammonium fluorosulfates:

$$ROSO_2F + (C_2H_5)_3N \rightarrow [(C_2H_5)_3NR]OSO_2F.$$

When these ammonium salts are heated, alkyldiethylamines are formed:

$$[(C_2H_5)_3NR]OSO_2F \xrightarrow{i^0} (C_2H_5)_2NR$$

Hence, alkyl fluorosulfates are more effective alkylating agents than chlorosulfuric and sulfuric esters.

#### EXPERIMENTAL

<u>Reaction of Tetrafluoro-2-hydroxyethane-</u> sulfonic  $\beta$ -Sultone with Methanesulfonyl Chloride. 11.5 g of methanesulfonyl chloride was added dropwise with stirring to 18.0 g of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone at room temperature. Fractionation of the mixture gave 18.7 g (95%) of trifluorovinyl chlorosulfate and 8.8 g (90%) of methanesulfonyl fluoride, b.p. 124-125°. Found %: F 19.10; S 32.44. CH<sub>3</sub>O<sub>3</sub>FS. Calculated %; F 19.38; S 32.68.

<u>Reaction of Tetrafluoro-2-hydroxyethane-</u> sulfonic  $\beta$ -Sultone with Sulfuryl Chloride. A mixture of 18.0 g of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone and 13.5 g of sulfuryl chloride was heated in an autoclave at 100° for 6 h. The autoclave was opened, and the contents were fractionated at atmospheric pressure. We obtained 2.5 g (21%) of sulfuryl chloride fluoride, 11.3 g (62.5%) of difluoro-(fluorosulfonyl)acetyl fluoride, 9.5 g (70%) of sulfuryl chloride, and 3.9 g (20%) of trifluorovinyl chlorosulfate. The products were identified by means of gas chromatography with the use of comparison substances.

<u>Reactions of Tetrafluoro-2-hydroxyethane-</u> sulfonic  $\beta$ -Sultone with Alkyl Chlorosulfates. A mixture of 0.1 mole of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone and 0.1 mole of the alkyl chlorosulfate was heated under reflux in a water bath. In the subsequent fractionation we isolated trifluorovinyl chlorosulfate and the corresponding alkyl fluorosulfate. The analyses of the alkyl fluorosulfates obtained are given in Table 3.

<u>Calculation of the Fluorosulfate Group.</u> The refraction of the fluorosulfate group was deduced from experimentally found values of density and refractive index for six unsubstituted alkyl fluorosulfates. For this purpose we determined the differences between the values found for the molecular refractions of the alkyl fluorosulfates and the known values of the alkyl groups. The calculated differences corresponding to values of the refraction of the fluorosulfate group were averaged, and the resulting value of  $R_{OSO_2}F$ , equal to 11.497, was used in the calculation of the molecular refractions of alkyl fluorosulfates (Table 4).

Hydrolysis of Alkyl Fluorosulfates. A weighed amount (0.1-0.2 g) of the preparation was dissolved in 25 ml of 0.1 N NaOH, and after 1 h the excess of alkali was

						I	2		Calci	ulated		$\Delta$ ]	MR	
Alkyl fl	uorosulf	ate	Foun	d MR	alk	xyl	os	O <sub>2</sub> F	M	R	er	$n^3$		%
CH <sub>3</sub> O	$SO_{2}F$		16.	940	5.	653	11.	287	17	.150	+ 0,	210		1.22
$C_2H_5C$	)SO <sub>2</sub> F		21.	813	10.	300	11.	513	21	.797	-0.	016		0.07
n-C <sub>3</sub> H	I7OSO2F		26.	450	14.	965	11.	485	26	.462	+0.	012		0,05
$n-C_4H$	$I_9OSO_2F$		31.	242	19.	585	11.	657	31	.082	0.	160		0,50
n-C <sub>5</sub> H	I11OSO2F	•	35.	724	24.	250	11.	474	35	.747	+ 0.	023		0.06
n–C <sub>6</sub> I	$-C_6H_{13}OSO_2F$ 40.421		421	28.	855	11.	566	40	.352	-0.	069		0.17	
TABI	LE 5				Aver	age	11.	497						
						-	R in R(	$OSO_2F$						_
Equi	lvalent	С	$H_3$	C	$_2H_5$	n-0	$C_{3}H_{7}$	n-C	$_4\mathrm{H}_9$	n-C	<sub>5</sub> H <sub>11</sub>	n-C <sub>e</sub>	<sub>3</sub> H <sub>13</sub>	_
Na Fl	lOH lloride	0. 0	98 96	] ]	L.02	1	L.01		.00 1 99		.01 97	0.	.99 98	-
**		FABLE	E 6	I ``		1		I ~		I				
		R-	C1	n-C <sub>3</sub> H <sub>7</sub> C1		$n-C_4H_9C1$		$n-C_5H_{11}C1$		$n-C_6H_{13}Cl$				
	_	Yield	,%	78	3	7	'5 72		2	75				
TABLE 7					dan da seconda da seco									
					Found	1, %					Calcul	ated, 🕅	1	

		Found, %		Calculated, %			
R <sub>4</sub> NOSO <sub>2</sub> F	N	F	S	N	F	S	
$\begin{array}{c} ({\rm C_2H_5})_3{\rm N}({\rm C_6H_{13}}){\rm OSO_2F} \\ ({\rm C_2H_5})_3{\rm N}({\rm C_5H_{11}}){\rm OSO_2F} \\ ({\rm C_2H_5})_3{\rm N}({\rm CH_3}){\rm OSO_2F} \end{array}$	$4.65 \\ 4.94 \\ 6.28$	$6.97 \\ 7.41 \\ 9.13$	$11.12 \\ 11.63 \\ 15.10$	$4.91 \\ 5.17 \\ 6.52$	$6.67 \\ 7.03 \\ 8.84$	$     11.22 \\     11.82 \\     14.87 $	

back-titrated with 0.1 N HCl to phenolphthalein (Table 5). Fluoride was absent in the hydrolyzate (test with zirconium-alizarin lake), but the fluorosulfate ion was present (tested by formation of nitron salt). The hydrolyzate was boiled with 20 ml of HCl (sp.gr. 1.10) for 2 h, and the fluoride content was determined thoriometrically; sulfate was detected in the solution.

<u>Reactions of Alkyl Fluorosulfates with Sodium Chloride</u>. 0.1 mole of the alkyl fluorosulfate was added dropwise slowly to 15 g of sodium chloride at room temperature. In the subsequent heating of the mixture a fraction was distilled off which yielded the alkyl chloride on redistillation; the alkyl chloride was identified from its boiling point, molecular weight, and halogen content (Table 6).

<u>Reactions of Alkyl Fluorosulfates with Triethylamine</u>. 0.1 mole of the alkyl fluorosulfate was added slowly with stirring to a solution of 0.1 mole of triethylamine in 20 ml of dry ether at  $-20^{\circ}$ . The resulting precipitate of the quaternary ammonium fluorosulfate was filtered off, washed with ether, and analyzed (Table 7).

When triethylmethylammonium fluorosulfate was heated above 100-120°, decomposition occurred and a fraction distilled off. Redistillation of this gave N-methyldiethylamine, b.p. 66-67°. Found %: N 15.91; mol. wt. 85.0.  $C_5H_{13}N$ . Calculated %: N 16.09; mol. wt. 87.1.

In an analogous way, from the triethylpentylammonium salt we isolated N,N-diethylpentylamine, b.p. 159-161°. Found %: N 10.32; mol. wt. 130.5. C<sub>9</sub>H<sub>21</sub>N. Calculated %: N 10.52; mol. wt. 133.3.

### CONCLUSIONS

1. In the reactions of tetrafluoro-2-hydroxyethanesulfonic  $\beta$ -sultone with methanesulfonyl chloride, with alkyl chlorosulfates, and with sulfuryl chloride trifluorovinyl chlorosulfate is formed together with the corresponding fluorosulfonyl compounds.

2. The reactions of fluorine-containing  $\beta$ -sultones with alkyl chlorosulfates provide a general method for the preparation of previously inaccessible alkyl fluorosulfates.

- 3. The main functional peculiarity of alkyl fluorosulfates is their great alkylating power.
- 4. It was deduced that the fluorosulfonyloxy group has a refraction  $\mathrm{R}_{\mathrm{OSO}_{2}\mathrm{F}}$  of 11.50.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of the first issue of this year.