FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

IV.* SULFOTRIOXIDIZING CAPACITY OF HEXAFLUOROISOBUTENYLIDENE SULFATE

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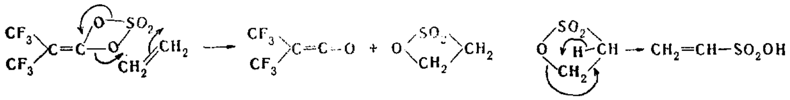
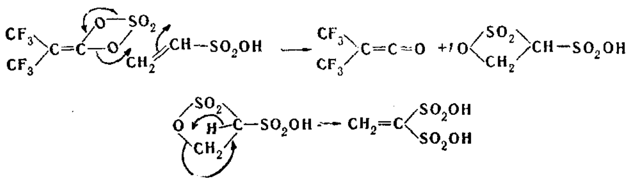
Hexafluoroisobutenylidene sulfate is a sulfotrioxidizing agent with respect to various olefins; methylenemethionic acid is formed in the case of ethylene, while the corresponding β-sulfones are formed in the case of tetrafluoroethylene and vinylidene fluoride. 2,2-Difluoro-2-hydroxyethanesulfonic acid sultone is characterized by a capacity for anionotropic transformations; a number of sulfoacetic acid derivatives were obtained on the basis of this sultone.

A method for the preparation of hexafluoroisobutenylidene sulfate and some of its properties, in particular its behavior with respect to alkali metal halides, water, ethers, and tertiary amines, were described in previous communications [1-3]. In all cases, the reagent was sulfotrioxidized and hexafluorodimethylketene was liberated. There is no doubt that this trend of these processes is explained by initial attack by the electrophilic sulfonyl group of the hexafluoroisobutenylidene sulfate that is directed to the electron-donor centers of the reagent molecules. It might have been assumed that this sort of attack is possible not only on the unshared p electrons of the halogen, oxygen, or nitrogen atoms but also on the collectivized π electrons of the multiple bonds. The validity of this assumption was confirmed by direct experiments, which are discussed in the present communication.

When ethylene is passed through liquid hexafluoroisobutenylidene sulfate, an exothermic reaction, as a result of which the ketene is liberated and methylenemethionic acid is formed, is observed. The formation of this acid can be described by the following sequence of reactions. Ethylene is sulfotrioxidized and 2-hydroxyethanesulfonic acid sultone is formed in the first step; the sultone, like other hydrogen-containing β-sultones, is inclined to undergo prototropic isomerization to give ethenesulfonic acid [4].



Since the reaction is accomplished in hexafluoroisobutenylidene sulfate solution, the ethenesulfonic acid undergoes further sulfotrioxidation to give 1-hydroxysulfonyl-2-hydroxyethanesulfonic acid sultone, which undergoes prototropic isomerization to methylenemethionic acid – the final product of the reaction.



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*See [1] for communication III.

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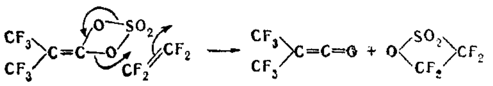
TABLE 1. 2,2-Difluoroethane β-Sultone and Products of Its Transformations

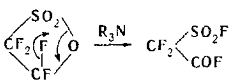
Compound	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found						Calculated						Yield, %
				found	calc.		C, %	H, %	F, %	S, %	equiv. wt. (KOH)	equiv. wt. (F ion)	C, %	H, %	F, %	S, %	equiv. wt. (KOH)	equiv. wt. (F ion)	
2,2-Difluoroethane β-sultone	55(15)	1,6630	1,3730	19,7	20,0	$C_2H_2F_2O_3S$	16,4	1,4	26,0	21,9	4,03	1,98	16,7	1,4	26,4	22,2	4,0	2,0	98
Fluorosulfonylacetyl fluoride	58(10)	1,6513	1,3800	20,6	20,2	$C_2H_2F_2O_3S$	16,7	1,3	26,5	—	4,02	1,96	16,7	1,4	26,4	—	4,0	2,0	97
Fluorosulfonylacetic acid	112(2)	—	—	—	—	$C_2H_3FO_4S$	16,4	2,5	12,9	22,0	3,08	1,02	16,9	2,1	13,4	22,5	3,0	1,0	64
Methyl fluorosulfonylacetate	99(10)	1,4600	1,4052	26,2	27,0	$C_3H_5FO_4S$	14,0	2,3	12,5	20,2	3,06	1,05	14,1	2,0	12,2	20,5	3,0	1,0	70
Ethyl fluorosulfonylacetate	102(10)	1,3402	1,4050	31,1	31,7	$C_4H_7FO_4S$	—	—	—	19,0	2,96	0,96	—	—	—	18,8	3,0	1,0	65
n-Propyl fluorosulfonylacetate	108(10)	1,2803	1,4105	35,7	36,3	$C_5H_9FO_4S$	—	—	10,6	—	3,08	1,02	—	—	10,3	—	3,0	1,0	45

The structure of the methylenemethionic acid was confirmed by IR spectroscopy and also by the results of alkalimetry and bromometry.

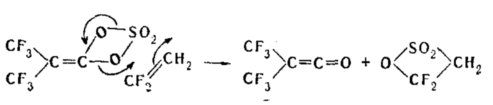
The reaction of hexafluoroisobutenylidene sulfate with tetrafluoroethylene is also accomplished under relatively mild conditions (40-50°); the reaction is accompanied by the liberation of the ketene and the formation of 2-hydroxy-1,1,2,2-tetrafluoroethanesulfonic acid sultone.



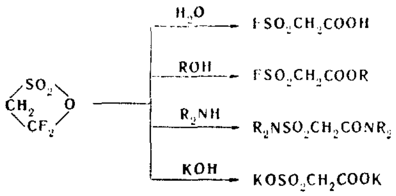
The structure of the tetrafluoro β-sultone was confirmed by F^{19} NMR spectroscopy, the results of alkaline hydrolysis, and isomerization to fluorosulfonyldifluoroacetyl fluoride [4].



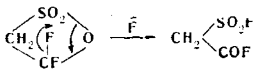
The ability of hexafluoroisobutenylidene sulfate to act as a mild sulfotrioxidizing agent with respect to such antipodes as ethylene and tetrafluoroethylene made it possible to hope for the possibility of obtaining β-sultones that previously could not be synthesized when free sulfur trioxide was used. For example, it is known that the reaction of liquid sulfur trioxide with vinylidene fluoride gives an unstable 2:1 adduct, to which the 2,2-difluoroethane β-pyrosultone structure [5, 6] was assigned. In contrast to these experiments, it was found that 2-hydroxy-2,2-difluoroethanesulfonic acid sultone is formed in quantitative yield when vinylidene fluoride is passed through hexafluoroisobutenylidene sulfate at 10-20°.



Fluorosulfonylacetic acid is formed in the neutral hydrolysis of 2,2-difluoroethane β-sultone, alcoholysis gives its esters, treatment with secondary amines gives diamides of sulfoacetic acid, and the action of aqueous alkalis gives sulfoacetic acid salts.



This sort of trend of the basic solvolysis of 2,2-difluoroethane β-sultone can be explained only by the fact that anionotropic conversion of the cyclic β-sultone to its linear isomer – fluorosulfonylacetyl fluoride – occurs in the first step of the process. The ability of the β-sultone to undergo this sort of isomerization was confirmed by direct experiment: fluorosulfonylacetyl fluoride is formed in quantitative yield when this compound is heated in the presence of potassium bifluoride.



Thus a number of sulfoacetic acid derivatives (Table 1) were obtained from 2,2-difluoroethane β-sultone. The structures of the compounds obtained were proved by various methods: PMR and F^{19} spectroscopy, alkalimetry,

TABLE 2. NMR Spectrometry*

Compound	PMR		F19 NMR		
	δ, ppm	$J_{H,F}$, Hz	δ, ppm	$J_{F,H}$, Hz	$J_{F,H}$, Hz
Tetrafluoroethane β-sultone	—	—	−14,3 t −23,7 t	— —	2,9 2,9
Fluorosulfonyldifluoroacetyl fluoride	—	—	−119,2 t −103,8 t 2,2 dd	— — —	5,1 5,1 5,1
2,2-Difluoroethane β-sultone	5,4 t	6,0	−3,0 t	6,1	—
Flurosulfonylacetyl fluoride	5,0 d	4,0	−138,0 dt −126,0 d	4,0 4,0	15,0 —
Fluorosulfonylacetic acid	—	—	−136,0 t	4,0	—
Methyl fluorosulfonylacetate	d, †	4,0	−138,0 t	4,0	—
Ethyl fluorosulfonylacetate	d †	4,0	−138,0 t	4,0	—
n-Propyl fluorosulfonylacetate	d †	4,0	−138,0 t	4,0	—
Sulfoacetic acid dimorpholide	5,2 s	—	—	—	—

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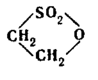
*Abbreviations: s is singlet, d is doublet, t is triplet, dd is doublet of doublets, and dt is doublet of triplets.

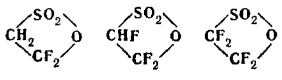
† The spectrum was recorded without a standard.

and thoriometry (Tables 1 and 2). Their formation in the reactions presented above indicates the anionotropic character of the reactivity of 2,2-difluoroethane β-sultone.

It is interesting to note that hydrogen-containing β-sultones are inclined to undergo prototropic transformations due to migration of hydrogen from the α position of the ring, while fluorine-containing β-sultones are inclined to undergo anionotropic transformations due to migration of fluorine from the β position of the ring [4]. However, if both hydrogen atoms in the α position and fluorine atoms in the β position are present simultaneously in the β-sultone molecule, the tendency for anionotropic transformations prevail. This phenomenon was previously observed in cases of the conversion of α-hydrotrifluoroethane β-sultone [4]; in the present communication, this same phenomenon was confirmed in cases of conversions of 2,2-difluoroethane β-sultone. The new method for the sulfotrioxidation of olefins examined in the present paper provides the prerequisites for the synthesis and further study of the reactivity of β-sultones of different types.



prototropic



anionotropic

EXPERIMENTAL

Methylenemethionic Acid. Dry ethylene was bubbled slowly into 14.6 g (0.057 mole) of hexafluoroisobutenylidene sulfate at 10-20°, during which hexafluorodimethylketene evolution, slight warming, and the formation of a crystalline precipitate were observed. The reaction stopped after solidification of the entire reaction mixture; 3.5-4 liters of ethylene was consumed, and 9 g of hexafluorodimethylketene was collected in a trap cooled with a mixture of acetone and dry ice. Recrystallization of the reaction mixture from carbon tetrachloride–dichloroethane (1 : 1) gave 4.5 g (85%) of methylenemethionic acid as white crystals that fumed in air. IR spectrum: ν_{SO_3} 1580 cm^{-1}. Found,%: C 12.7; H 2.6; S 33.7. Equiv.wt. (KOH) 1.97; (Br_2) 0.95. $C_2H_4O_6S_2$. Calculated,%: C 12.8; H 2.1; S 34.0. Equiv. wt. (KOH) 2.0; (Br_2) 1.0.

Tetrafluoroethene β-Sultone. Tetrafluoroethylene was bubbled slowly into 12.9 g (0.05 mole) of hexafluoroisobutenylidene sulfate at 40-50° (with a reflux condenser) until the evolution of hexafluorodimethylketene, which was condensed in a trap cooled with a mixture of acetone and dry ice, ceased; 8.9 g of the ketene was collected. Fractionation of the reaction mixture gave 8.7 g (96%) of tetrafluoroethane β-sultone, which was identified from its physical properties, by F^{19} NMR spectroscopy, and from the results of alkaline hydrolysis. Found: Equiv. wt. (KOH) 3.95; (F ion) 1.96. $C_2F_4O_3S$. Calculated: Equiv. wt. (KOH) 4.0; (F ion) 2.0.

Two to three drops of triethylamine were added to 9.0 g of tetrafluoroethane β-sultone in a flask equipped with a dry-ice reflux condenser; vigorous effervescence of the mixture was observed. Subsequent fractionation gave 8.4 g (89%) of fluorosulfonyldifluoroacetyl fluoride, which was identified from its physical properties [7], by F^{19} NMR spectroscopy, and from the results of alkaline hydrolysis. Found: Equiv. wt. (KOH) 4.05; (F ion) 2.03. $C_2F_4O_3S$. Calculated: Equiv. wt. (KOH) 4.0 (F ion) 2.0.

2,2-Difluoroethane β-Sultone. Vinylidene fluoride was bubbled slowly into 25.8 g (0.1 mole) of hexafluoroisobutenylidene sulfate at 10-20° (with a reflux condenser) until hexafluorodimethylketene evolution ceased; 17.8 g of the ketene was collected. Fractionation of the reaction mixture gave 14.1 g of 2,2-difluoroethane β-sultone (Table 1).

Fluorosulfonylacetic Acid. A 0.9-g (0.05 mole) sample of water was added by drops slowly with shaking to 7.2 g (0.05 mole) of 2,2-difluoroethane β-sultone in a Teflon apparatus. The mixture was then heated on a water bath until the hydrogen fluoride had been completely removed (30 min). Subsequent fractionation gave 4.6 g of fluorosulfonylacetic acid, which was crystallized to give needles with mp 37° (Table 1).

Alkyl Fluorosulfonylacetates (Table 1). A 0.05-mole sample of alcohol was added to 7.2 g (0.05 mole) of the β-sultone in a Teflon apparatus, and the mixture was refluxed on a water bath for 1 h. It was then washed twice with ice water, and the lower layer was separated, dried with magnesium sulfate, and fractionated.

Sulfoacetic Acid Dimorpholide. A solution of 8.7 g (0.1 mole) of morpholine in 10 ml of ether was added to a solution of 3.6 g (0.025 mole) of the β-sultone in 5 ml of diethyl ether, during which a colorless crystalline precipitate formed. The precipitate was recrystallized from toluene to give 4.6 g (66%) of sulfoacetic acid dimorpholide as prisms with mp 143°. Found,%: N 10.1. $C_{10}H_{18}N_2O_5S$. Calculated,%: N 10.0.

Fluorosulfonylacetyl Fluoride. A mixture of 7.2 g (0.05 mole) of 2,2-difluoroethane β-sultone and 0.3 g of potassium bifluoride was heated on a water bath for 2 h. Subsequent fractionation gave 7.0 g of fluorosulfonylacetyl fluoride (Table 1).

Alkalimetry. A weighed sample of the preparation (0.05-0.1 g) was dissolved in 10-20 ml of 0.1 N potassium hydroxide, and the excess alkali was titrated after 10-15 min with 0.1 N hydrochloric acid with respect to phenolphthalein. The percentage of fluoride ions in the hydrolyzate was determined by a thoriometric method. The results of analysis are presented in Table 1.

Spectrometry. The F^{19} NMR and PMR spectra were recorded with a Hitachi-Perkin Elmer model R-20 spectrometer with a field intensity of 14,092 G. The F^{19} chemical shifts were measured in carbon tetrachloride solution with an external standard and are presented in parts per million of the field relative to trifluoroacetic acid; the H^1 chemical shifts were recorded in the same solvent with an internal standard (tetramethylsilane) and are presented relative to the latter (see Table 2).

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