FLUORINE-CONTAINING β-SULTONES

XXI. DERIVATIVES OF α-FLUOROSULFONYLTETRAFLUOROPROPIONIC ACID

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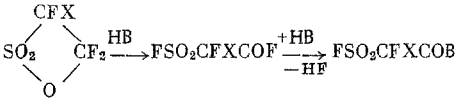
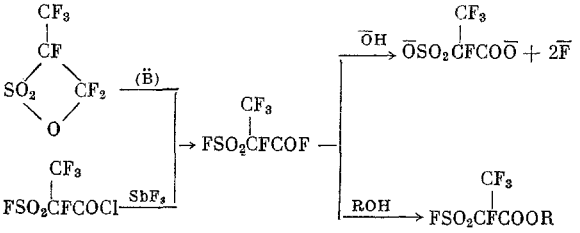
It has been shown previously [1] that the corresponding derivatives of α-fluorosulfonylpolyfluorocarboxylic acids are formed on reaction of fluorine-containing β-sultones with nucleophilic compounds. The process includes an intermediate isomerization of the cyclic β-sultones into linear α-fluorosulfonylcarboxylic acid fluorides and reaction of the latter with the nucleophilic reagent [2].

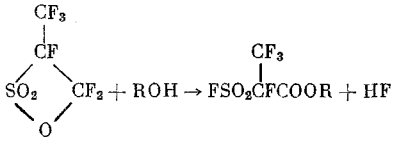


The results of the transformations of hexafluoropropane-2-β-sultone which are described in the present communication can be considered from the same point of view.

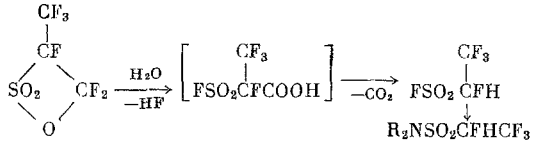
Thus, hexafluoropropane-2-β-sultone is isomerized into α-fluorosulfonyltetrafluoropropionyl fluoride on heating, under the action of potassium fluoride, and also in the presence of hydrogen fluoride or ethers. The structure of the linear bisacyl fluoride was confirmed by counter synthesis, by the results of alkalimetry, and by its conversion into methyl α-fluorosulfonyltetrafluoropropionate.



Upon reaction of hexafluoropropane-2-β-sultone with alcohols, the appropriate esters of α-fluorosulfonyltetrafluoropropionic acid are formed in quantitative yield.



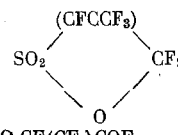
α-Fluorosulfonyltetrafluoropropionic acid is formed on hydrolysis of hexafluoropropane-2-β-sultone; this is decarboxylated under the reaction conditions and is converted thereupon into α-hydrotetrafluoroethanesulfonyl fluoride. The structure of the latter compound was confirmed by results of alkalimetry and by conversion into the corresponding amide.



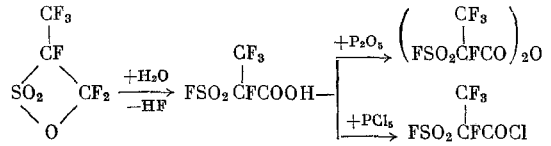
The formation of α-fluorosulfonyltetrafluoropropionic acid on hydrolysis of hexafluoropropane-2-β-sultone was established by the isolation of the anhydride or acid chloride of this acid when a mixture of

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1754-1758, August, 1967. Original article submitted April 9, 1966.

TABLE 1

Compound	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}
	46.5	1.6670	1.3000
$FSO_2CF(CF_3)COF$	42.5	1.7060	1.28
$FSO_2CF(CF_3)COCl$	70	1.5634	1.3200
$[FSO_2CF(CF_3)CO-]_2O$	152	1.7738	1.3335
$FSO_2CF(CF_3)COOCH_3$	118.5	1.5600	1.3415
$FSO_2CF(CF_3)COOC_2H_5$	131.5	1.4743	1.3448
$FSO_2CF(CF_3)COOC_3H_7$-n	148	1.4022	1.3520
$FSO_2CF(CF_3)COOC_4H_9$-n	72(20)	1.3700	1.3630
$FSO_2CF(CF_3)COOC_5H_{11}$-n	64(8)	1.3751	1.3700
$FSO_2CF(CF_3)COOC_6H_{13}$-n	86(11)	1.2900	1.3760
$FSO_2CF(CF_3)COOC_6H_{11}$-cyclo	110(2)	1.3902	1.3885
FSO_2CFHCF_3	60	1.6496	1.3000
$(C_2H_5)_2NSO_2CFHCF_3$	89(3)	1.3091	1.3915

equimolecular quantities of the β-sultone and water was treated with phosphorus pentoxide or phosphorus pentachloride, respectively.



Thus, the corresponding derivatives of α-fluorosulfonyltetrafluoropropionic acid are formed in every case investigated upon reaction of hexafluoropropane-2-β-sultone with nucleophilic compounds. The physical properties of the compounds obtained are given in Table 1.

EXPERIMENTAL

Isomerization of Hexafluoropropane-2-β-sultone. Into a 100-ml steel autoclave was placed 23.0 g of hexafluoropropane-2-β-sultone. The autoclave was heated at 150-160° for 1 h, after which it was cooled and opened. The contents were fractionated in a column (23 theoretical plates). The yield of α-fluorosulfonyltetrafluoropropionyl fluoride obtained was 16.1 g (70%). Found %: C 15.83; F 49.02; S 14.03. Mol. wt. 233.5. $C_3O_3F_6S$. Calculated %: C 15.60; F 49.52; S 13.93. Mol. wt. 230.2.

To 23.0 g of hexafluoropropane -2-β-sultone, with ice-cooling, anhydrous hydrogen fluoride was added dropwise until the vigorous reaction ceased (10-15 drops). The mixture was fractionated after addition of 1 g of potassium fluoride. α-Fluorosulfonyltetrafluoropropionyl fluoride (16.4 g, 71%) was isolated.

Di-n-butyl ether (1-1.5 ml) was added dropwise to 23.0 g of hexafluoropropane-2-β-sultone until the vigorous reaction ceased. α-Fluorosulfonyltetrafluoropropionyl fluoride (18.4 g) was isolated by fractionation.

α-Fluorosulfonyltetrafluoropropionyl fluoride was obtained similarly from hexafluoropropane-2-β-sultone in the presence of dioxane, chlorex(bis-2-chloroethyl ether) or dichlorodimethyl ether, in yields of 75, 75, and 83%, respectively.

Preparation of α-Fluorosulfonyltetrafluoropropionyl Fluoride. A mixture of 24.7 g of α-fluorosulfonyltetrafluoropropionyl chloride and 12.0 g of sublimed antimony fluoride was heated on a boiling water bath under a fractionating column; a colorless liquid distilled out thereupon. α-Fluorosulfonyltetrafluoropropionyl fluoride (19.5 g, 85%) was isolated by repeated fractionation of the latter.

Methyl α-fluorosulfonyltetrafluoropropionate was isolated in 90% yield by solution of the α-fluorosulfonyltetrafluoropropionyl fluoride in methanol, subsequent washing with water, drying over $MgSO_4$ and fractionation.

Alcoholysis of Hexafluoropropane-2-β-sultone. To 23.0 g of the β-sultone, with cooling, was slowly added dropwise 0.10-0.12 mole of the dry alcohol; warming up of the solution was noted thereupon, plus evolution of hydrogen fluoride. The mixture was washed twice with water; the lower layer

TABLE 2

$FSO_2CF(CF_3)COOR$ R	Yield, %	Found			Empirical formula	Calculated		
		F, %	S, %	MR		F, %	S, %	MR*
CH_3	90	39.78	13.04	32.66	$C_4H_3O_4F_5S$	39.19	13.23	32.54
C_2H_5	85	37.45	12.30	36.88	$C_5H_5O_4F_5S$	37.10	12.49	37.18
n-C_3H_7	88	35.52	11.62	41.67	$C_6H_7O_4F_5S$	35.20	11.84	41.85
n-C_4H_9	78	33.04	11.48	46.13	$C_7H_9O_4F_5S$	33.44	11.24	46.27
n-C_5H_{11}	73	32.75	10.94	51.29	$C_8H_{11}O_4F_5S$	32.30	10.72	51.13
n-C_6H_{13}	75	30.54	10.26	55.54	$C_9H_{13}O_4F_5S$	30.34	10.26	55.74
cyclo-C_6H_{11}	70	30.33	10.10	52.71	$C_9H_{11}O_4F_5S$	30.65	10.32	52.56

*In calculation we used a refractivity value of 10.54 [3] for the fluorosulfonyl group

TABLE 3

Compound	Found, equiv.		
	KOH	F	Cl
α-Fluorosulfonyltetrafluoropropionic anhydride	6.08	2.06	-
α-Fluorosulfonyltetrafluoropropionyl chloride	3.96	0.97	0.96
α-Fluorosulfonyltetrafluoropropionyl fluoride	4.06	1.92	-
Methyl α-fluorosulfonyltetrafluoropropionate	2.94	1.03	-
Ethyl α-fluorosulfonyltetrafluoropropionate	3.03	1.05	-
n-Propyl α-fluorosulfonyltetrafluoropropionate	2.90	0.99	-
n-Butyl α-fluorosulfonyltetrafluoropropionate	2.93	1.06	-
n-Amyl α-fluorosulfonyltetrafluoropropionate	2.93	1.04	-
n-Hexyl α-fluorosulfonyltetrafluoropropionate	3.00	1.07	-
Cyclohexyl α-fluorosulfonyltetrafluoropropionate	3.08	0.92	-
α-Hydrotetrafluoroethanesulfonyl fluoride	1.94	1.05	-

was separated and dried over $MgSO_4$. The appropriate ester of α-fluorosulfonyltetrafluoropropionic acid was isolated by fractionation. Yields and analyses of the compounds are given in Table 2.

Hydrolysis of Hexafluoropropane-2-β-sultone. Water (10 ml) was slowly added dropwise to 23.0 g of the β-sultone with stirring and ice-cooling. The lower layer was separated, washed with ice water, dried over $MgSO_4$ and fractionated. α-Hydrotetrafluoroethanesulfonyl fluoride (17.1 g, 93%) was isolated. Found %: C 13.22; F 51.96; S 17.46. Mol. wt. 180.5. $C_2HO_2F_5S$. Calculated %: C 13.02; F 51.65; S 17.35. Mol. wt. 184.2.

A solution of 16.0 g of diethylamine in 20 ml of ether was added dropwise with ice-cooling and stirring to a solution of 18.4 g of α-hydrotetrafluoroethanesulfonyl fluoride in 20 ml of absolute ether. The mixture was warmed to room temperature and was diluted with 20 ml of ether. The ether layer was separated, dried over $MgSO_4$ and fractionated. α-Hydrotetrafluoroethanesulfonic acid diethylamide (15.7 g, 66%) was isolated. Found %: N 5.63. $C_6H_{11}O_2NF_4S$. Calculated %: N 5.45.

Preparation of α-Fluorosulfonyltetrafluoropropionic Anhydride. To a solution of 23.0 g of hexafluoropropane-2-β-sultone in 25 ml of methylene chloride, placed in a Teflon reactor, was slowly added 1.8 g of water, dropwise, with stirring and cooling to −10°; and then 14.2 g of phosphorus pentoxide was added rapidly. The mixture was heated at 50° for 2 h under reflux. By subsequent fractionation, 15.6 g (71%) of α-fluorosulfonyltetrafluoropropionic anhydride was isolated. Found %: F 42.86; S 14.51. Mol. wt. 430.5. $C_6O_7F_{10}S_2$. Calculated %: F 42.40; S 14.27. Mol. wt. 438.2.

Preparation of α-Fluorosulfonyltetrafluoropropionyl Chloride. Similarly, by introduction of 41.7 g of phosphorus pentachloride into the solution of the hexafluoropropane-2-β-sultone hydrolyzate, subsequent heating of the reaction mixture, and fractionation, there was obtained 18.5 g (75%) of α-fluorosulfonyltetrafluoropropionyl chloride. Found %: F 39.01; Cl 14.10; S 13.22. Mol. wt. 240.5. $C_3O_3F_5ClS$. Calculated %: F 38.48; Cl 14.37; S 12.96. Mol. wt. 246.6.

A mixture of 24.7 g of α-fluorosulfonyltetrafluoropropionyl chloride and 12.0 g of sublimed antimonyl trifluoride was heated at 80-90° under a column. α-Fluorosulfonyltetrafluoropropionyl fluoride (19.5 g, 85%) was isolated by fractionation of the distillate driven off over antimony trifluoride. α-Hydrotetrafluoroethanesulfonyl fluoride was isolated in 78% yield by treatment of α-fluorosulfonyltetrafluoropropionyl chloride with water and subsequent fractionation.

Alkaline Hydrolysis of Compounds Prepared. A 0.1-0.2 g samples of the preparation was dissolved in 25-50 ml of 0.1 N KOH; the excess alkali was titrated to phenolphthalein with 0.1 N H_2SO_4. The fluoride ion content was determined in the hydrolyzate by thoriometry, and the chloride ion by argentometry. Results of analyses are given in Table 3.

CONCLUSIONS

1. Hexafluoropropane-2-β-sultone is isomerized to α-fluorosulfonyltetrafluoropropionyl fluoride under the action of nucleophilic agents.

2. Some derivatives of α-fluorosulfonyltetrafluoropropionic acid have been obtained; the acid fluoride and acid chloride, the anhydride, and some esters.

3. α-Hydrotetrafluorothanesulfonyl fluoride has been prepared by decarboxylation of α-fluorosulfonyltetrafluoropropionic acid.

LITERATURE CITED

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2. G. A. Sokol'skii, M. A. Belaventsev, and I. L. Knunyants, Izv. AN SSSR, ser. khim., 1967, 1524.
3. G. A. Sokol'skii and I. L. Knunyants, Izv. AN SSSR, ser. khim., 1961, 1468.