FLUORINE - CONTAINING β - SULTONES COMMUNICATION 19. REACTIVITY OF DERIVATIVES OF TRIFLUOROVINYL HYDROGEN SULFATE

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We have previously reported on the preparation of the acid chloride and esters of trifluorovinyl hydrogen sulfate [1-3]. The structure of these compounds was proved by the results of their alkaline hydrolysis, in which the consumption of alkali and the content of halide ions (argentometry and thoriometry) and glyoxylic acid (iodometry) in the hydrolyzate were determined.

 $CISO_2OCF = CF_2 + 6N_aOH \rightarrow NaCl + Na_2SO_1 + 3NaF + HCOCOOH + 2H_2O$ $ROSO_2OCF = CF_2 + 4N_aOH \rightarrow ROSO_2ONa + 3NaF + HCOCOOH + H_2O$

The course of the alkaline hydrolysis of derivatives of trifluorovinyl hydrogen sulfate indicates that the initial object of nucleophilic attack by the hydroxyl ion is the difluoromethylene group. This is possible only with a deficiency of electron density on the 2-carbon atom of the trifluorovinyl group. Polarization of this character in the double bond arises from the conjugation effect due to the electron-attracting action of the sulfonyl group:



It could be supposed that an analogous phenomenon would be characteristic also for reactions of derivatives of trifluorovinyl hydrogen sulfate with nucleophilic compounds. In this communication we examine the reactions of the acid chloride and esters of trifluorovinyl hydrogen sulfate with various reagents. It was found that neither the acid chloride nor the esters of trifluorovinyl hydrogen sulfate react with bromine, even with heating to 60–80°, and also they do not polymerize in presence of benzoyl peroxide and when heated to 180–200° in an autoclave. The inertness of derivatives of trifluorovinyl hydrogen sulfate toward electrophilic reagents is indicative of their electron-acceptor power and indirectly confirms the above-stated hypothesis concerning the character of the polarization of the double bond of the trifluorovinyl group.

As was expected, the reactivity of derivatives of trifluorovinyl hydrogen sulfate is manifested only toward nucleophilic reagents—amines, alcohols, and even acids. In the treatment of trifluorovinyl chloro-sulfate with diethylamine reaction is so vigorous that it is impossible to isolate the initial reaction products. In this experiment we isolated only the product of the degradation of the original compound—tetraethylsulfamide.

The reactions of alkyl trifluorovinyl sulfates with alcohols, which were conducted by heating equimolecular mixtures of the reactants for many hours, led to addition products containing an alkoxy group on the 2-carbon atom:

$$ROSO_2OCF = CF_2 + R'OH \rightarrow ROSO_2OCFHCF_2OR'$$

The structure of the adduct, and therefore the orientation in the addition, was proved by the alkalimetric method with subsequent determination of fluoride and glyoxylic acid in the hydrolyzate:

$$\begin{split} \text{ROSO}_2\text{OCFHCF}_2\text{OR}' + 4\text{NaOH} &\rightarrow \text{ROSO}_2\text{ONa} + 3\text{NaF} + \\ &+ \text{HCOCOOH} + \text{R'OH} + \text{H}_2\text{O} \end{split}$$

The reactions of trifluorovinyl chlorosulfate with alcohols go already at room temperature; the result depends on the amount of the alcohol taken. When only 1 molecular proportion of the alcohol is used,

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replacement of a fluorine atom of the difluoromethylene group by alkoxyl occurs. When double the amount of the alcohol is used, subsequent addition of the nucleophile at the double bond occurs. The stagewise character of the process is evident from the fact of the isolation of the same adduct in the treatment of the initially formed substitution product with the alcohol.

$$ClSO_2OCF = CF_2 + ROH \rightarrow ClSO_2OCF = CFOR + HF$$

$$ClSO_2OCF = CFOR + ROH \rightarrow ClSO_2OCFHCF(OR)_2$$

The structure of both alcoholysis products from trifluorovinyl chlorosulfate were proved by the alkalimetric method.

In the reaction of trifluorovinyl chlorosulfate with acetic acid the addition product is formed:

$$ClSO_2OCF = CF_2 + CH_3COOH \rightarrow ClSO_2OCFHCF_2OCOCH_3.$$

It is interesting that an adduct of analogous type was obtained earlier [1] in the reaction of trifluorovinyl chlorosulfate with chlorosulfuric acid:

$$ClSO_2OCF = CF_2 + ClSO_2OH \rightarrow ClSO_2OCFHCF_2OSO_2Cl$$

The above examples of the reactivity of the esters and acid chloride of trifluorovinyl hydrogen sulfate confirm the hypothesis about the character of the polarizability of the double bond and convincingly support the existence of conjugation between the trifluorovinyl and sulfonyl groups. It is extremely interesting that in alcoholysis and acidolysis reactions trifluorovinyl chlorosulfate is characterized by the lability of the double bond and the stability of the chlorosulfonyl group. Another example of the high stability of the chlorine-sulfonyl bond is found in the absence of reaction between trifluorovinyl chlorosulfate and hydrogen fluoride, potassium fluoride, potassium hydrogen difluoride, and copper and silver fluorides even after many hours in an autoclave at 100-120°.

Replacement of the chlorine atom in the molecule of trifluorovinyl chlorosulfate by fluorine occurs only when this compound is heated to 80-100° with anhydrous zinc fluoride. However, instead of the expected trifluorovinyl fluorosulfate we isolated the isomeric difluoro(flurosulfonyl)acetyl fluoride which was identified by various method (gas chromatography, alkalimetry, conversion into the corresponding ester and anilide):

$$ClSO_2OCF = CF_2 \xrightarrow{ZnF} FSO_2CF_2COF$$

The formation of difluoro(fluorosulfonyl)acetyl fluoride is undoubtedly a halogen-exchange reaction: trifluorovinyl fluorosulfate is formed in the first place, and this then undergoes rearrangement under the conditions of the process (80-100°). The possibility of the rearrangement of trifluorovinyl fluorosulfate follows from the already examined lability of the double bond due to the conjugation effect:



The possibility is not excluded that the rearrangement is an intermolecular process initiated by the "wall effect":



It is interesting that this rearrangement is observed only in the case of trifluorovinyl fluorosulfate, whereas alkyl trifluorovinyl sulfates and trifluorovinyl chlorosulfates are much more stable compounds: the former are stable up to 150-180°, and the chlorosulfate is stable up to 200-230°. This difference in the stabilities of derivatives of trifluorovinyl hydrogen sulfate is probably determined by difference in the induction effects of substituents on the sulfonyl group. It is evident that the I effect of an alkoxy group or a chlorine atom produces insufficient intensification of the effect of the sulfonyl group for the realization of the conjugation of the electron pairs: the π component of the carbon-carbon double bond and the σ oxygen-sulfonyl bond. The more powerful I effect of the fluorine is able to ensure the occurrence of this translocation of bonds, as a result of which rearrangement of trifluorovinyl fluorosulfate occurs.

ROSO2OCFHCF2OR/	$\substack{\substack{\mathbf{R}=\mathbf{C}_{2}\mathbf{H}_{5}\\\mathbf{R}'=\mathbf{C}_{2}\mathbf{H}_{5}}$	$\begin{array}{c} \mathbf{R} = \mathbf{C}_{2}\mathbf{H}_{5} \\ \mathbf{R}' = \mathbf{C}_{7}\mathbf{H}_{15} \cdot n \end{array}$	$\begin{array}{c} \mathbf{R} = \mathbf{C}_{4}\mathbf{H}_{9} \cdot n \\ \mathbf{R}' = \mathbf{C}_{4}\mathbf{H}_{9} \cdot n \end{array}$
Yield, %	56	46	52
B.p., [°] C (p, mm) d ²⁰ ₄ n ²⁰ _D	70—71 (25) 1.4472 1.3750	110—111 (4) 1.1900 1.3857	85—86 (3) 1,1182 1.3875
Found	28.36	41.05	38,93
C, % Calculated	28,56	41.29	39,11
Found H, % Calculated	4.14	6.30 6.57	6.00 6.21
Found F, % Calculated	22.92 22.59	17.95 17.69	18.83 18.49
Found S,% Calculated	12.92	10.20 9.99	10.72
Amount: of alkali (equiv) required of hydrolyzable fluorine of iodine (equiv) required	4.12 3.05 1,93	3,83 2.83 2.09	3.88 2.93 2.06

TABLE 1

EXPERIMENTAL

<u>A minolysis of Trifluorovinyl Chlorosulfate</u>. A solution of diethylamine in dry ether (1:1) was added slowly with stirring to 0.1 mole of trifluorovinyl chlorosulfate at 0° until reaction no longer occurred; 0.32-0.36 mole of the amine was consumed. The precipitate formed was filtered off. The filtrate was fractionated, first at reduced, and then at atmospheric pressure. We isolated tetraethyl-sulfamide in 45% yield; b.p. 248-250°. Found: N 13.73; S 15.18%. $C_8H_{20}O_2N_2S$. Calculated: N 13.46; S 15.38%.

<u>Alcoholysis of Alkyl Trifluorovinyl Sulfates</u>. A mixture of 0.1 mole of the alkyl trifluorovinyl sulfate and 0.1 mole of the anhydrous alcohol was heated at 70-100° for 3 h. By subsequent fractionation at reduced pressure we isolated the corresponding 2-alkoxy-1,2,2-trifluoroethyl alkyl sulfate as a colorless oil. The yields, physical properties, and analyses of the compounds obtained are given in Table 1.

Alcoholysis of Trifluorovinyl Chlorosulfate. 0.1 mole of the alcohol was added slowly with stirring to 0.1 mole of trifluorovinyl chlorosulfate at 0°. Dry nitrogen was then passed through the mixture for 3 h, and the mixture was fractionated at reduced pressure. We isolated the corresponding 2-alkoxydifluorovinyl chlorosulfate as a colorless oil (Table 2).

0.1 mole of the alcohol was added slowly with stirring to 0.1 mole of the 2-alkoxydifluorovinyl chlorosulfate at 20°. After 3-4 h the mixture was fractionated under reduced pressure. We isolated the corresponding 2,2-dialkoxy-1,2-difluoroethyl chlorosulfate as a colorless oil (see Table 2).

By reaction between 0.1 mole of trifluorovinyl chlorosulfate and 0.2 mole of the alcohol we obtained the corresponding 2,2-dialkoxy-1,2-difluoroethyl chlorosulfate.

<u>Acidolysis of Trifluorovinyl Chlorosulfate</u>. 0.1 mole of acetic acid was added to 0.1 mole of trifluorovinyl chlorosulfate at 20-25°. After 2 h the mixture was fractionated. Trifluoroethylene acetate chlorosulfate, acetic acid, and chlorosulfuric acid were isolated. Found: C 18.90; H 1.81; F 21.90; Cl 13.52; S 12.27%. $C_4H_4O_5F_3$ ClS. Calculated: C 18.72; H 1.58; F 22.22; Cl 13.82; S 12.51%. Yield 74%. The adduct is a colorless oil; b.p. 92-93° (10 mm); d_4^{20} 1.7205; n_D^{20} 1.4005. It is soluble in organic solvents and aqueous alkalies. No of equivalents found or required: alkali 6.05; fluoride 2.88; chloride 1.03; iodine 1.93.

Compound	CISO20CF=CFOR		ClSO2OCFHCF(OR)2	
	R=CH ₃	R=C4Hg-n	R=CH ₃	$R = C_4 H_9 - n$
Yield, %	85	80	66	61
B.p., °C (p, mm) d _{4 20} n _D	67 (21) 1.5889 1.3870	60 (2) 1.3758 1.4000	56 (15) 1,5010 1,3920	80 (2) 1.0081 1.4165
Found C, % _Calculated	17.53 17.27	28.31 28.06	19.81 20.00	36.62 36.98
Found H, % <u>Calculate</u> d	1.6 9 1.43	3.8 2 3.62	2.70 2.94	5.66 5.89
Found F, % Calculated	18.68 18.21	15.52 15.16	16.16 15.82	12.02 11.72
Found Cl, % Calculated	16.62 16.98	13.92 14.14	14.98 14.76	11.15 10.91
Found S, % Calculated	15.13 15.37	12.52 12.79	13.70 13.35	10.15 9.87
Amount: of alkali (equiv) required of hydrolyzable fluorine "chlorine of iodine (equiv) required	5.08 2,06 0,94 1,94	4.90 2.08 0.98 2.06	5.12 1.92 1.03 2.04	5.16 1.88 1.06 2,10

TABLE 2

<u>Reaction of Trifluorovinyl Chlorosulfate with Zinc Fluoride</u>. A mixture of 20 g of trifluorovinyl chlorosulfate and 10 g of anhydrous zinc fluoride was heated in a steel autoclave at 80-100° for 2 h. The autoclave was then cooled to -78°, opened, connected to a trap cooled to -78°, and warmed up gradually to 0°. 3.6 g of gaseous products came off and were condensed in the trap: they consisted of fluorine- and sulfur-containing compounds, among which by means of gas chromatography [4] we found sulfur dioxide, sulfuryl fluoride, and sulfuryl chloride fluoride.

The residue of the reaction mixture was fractionated. We isolated 6.1 g (33%) of difluoro(fluro-sulfonyl)acetyl fluoride, identified by means of alkalimetry and gas chromatography [4] and also by successive conversion into ethyl difluoro(flurosulfonyl)acetate [5] and 2,2-difluoro-2-(fluorosulfonyl)acet-anilide [6].

CONCLUSIONS

1. The reactivity of derivatives of trifluorovinyl hydrogen sulfate is determined by the conjugation of the trifluorovinyloxy and sulforyl groups.

2. Ey a halogen-exchange reaction with trifluorovinyl chlorosulfate difluoro(flurosulfonyl)acetyl fluoride was obtained. Its formation is explained by the rearrangement of the intermediate product-tri-fluorovinyl fluorosulfate.

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