FLUORO-CONTAINING β-SULTONES

COMMUNICATION 44. SULFOTRIOXIDATION OF 1,1-BIS(METHOXY)HEXAFLUOROISOBUTYLENE

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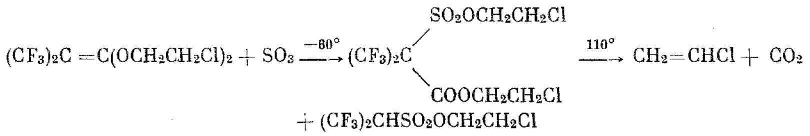
The reaction of 1,1-bis-(β-chloroethoxy)hexafluoroisobutylene with SO_3, which leads to the β-chloroethyl ester of hexafluoro-2-propanesulfonic acid, was described in a previous communication [1]. It was postulated that the unstable diester of α-sulfohexafluoroisobutyric acid is formed as an intermediate, which eliminates vinyl chloride and CO_2 when heated



$$(CF_3)_2C=C(OCH_2CH_2Cl)_2 + SO_3 \xrightarrow{-60^\circ} (CF_3)_2C(SO_2OCH_2CH_2Cl)(COOCH_2CH_2Cl) \xrightarrow{110^\circ} CH_2{=}CHCl + CO_2 + (CF_3)_2CHSO_2OCH_2CH_2Cl$$

The lability of the intermediate diester is evidently related to the mobility of the β-H atom of the alkoxyl radical. In this connection it seemed expedient to study the sulfotrioxidation of bis(alkoxy) substituted olefins that contain alcohol moieties devoid of the β-hydrogen.

As the study object we selected 1,1-bis(methoxy)hexafluoroisobutylene, which was described previously as being the product of the two-step alcoholysis of octafluoroisobutylene, with isolation of the intermediate methyl heptafluoroisobutylene ester [2]. It proved that the bis(methoxy) derivative can be obtained much more simply and in higher yield (>75%), without isolating the monoester, by the direct treatment of octafluoroisobutylene with sodium methylate at −30°C

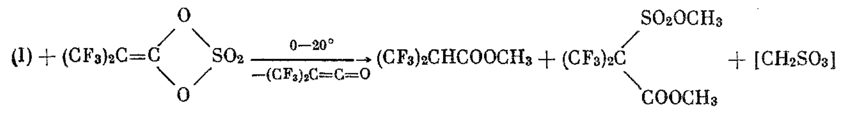
$$(CF_3)_2C{=}CF_2 + 2CH_3ONa \rightarrow \underset{(I)}{(CF_3)_2C{=}C(OCH_3)_2} + 2NaF$$

In the present paper we used free SO_3 and its adduct with hexafluorodimethylketene, namely hexafluoroisobutenylidene sulfate [3], as the sulfotrioxidating agents.

The reaction of (I) with SO_3 in Freon-22 solution is realized even at −60° and leads to methyl α-hydrohexafluoroisobutyrate in 94% yield

$$(I) + SO_3 \xrightarrow{-60^\circ} (CF_3)_2CHCOOCH_3 + [CH_2SO_3]$$

In the case of hexafluoroisobutenylidene sulfate the reaction is less exothermic and at 0-20° is accompanied by the elimination of hexafluorodimethylketene. Besides the latter, methyl α-hydrohexafluoroisobutyrate and dimethyl α-sulfohexafluoroisobutyrate were isolated from the reaction mixture; the yield of each of these esters is 50%



Besides the indicated products, in both cases we observed the formation of a white vaseline-like substance of the sulfonate type (is not oxidized by iodine), which is insoluble in water and has limited solubility in organic solvents, and which is apparently the α-polysultide: $[-CH_2-SO_2-O-]_n$. The obtained

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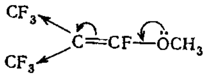
diester is relatively heat stable, which excludes the possibility of its conversion to the monoester under the reaction conditions.

The simultaneous formation of two esters is undoubtedly the result of parallel transformations, which can be explained by the intermediate participation of compounds of the sulfate type. Indirect evidence in support of such a premise are the known facts [4-8] that deal with the temperature conditions for the sulfotrioxidation of certain olefins and ethers (Table 1).

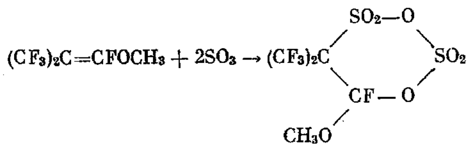
TABLE 1

Compound	Temperature of reaction with SO_3, °C	Literature reference
$CF_2{=}CF_2$	40	[4]
$CF_3CF{=}CF_2$	80	[4]
$(CF_3)_2C{=}CF_2$	>120	[5]
$(CF_3)_2C{=}CFOCH_3$	−30	[6]
$(CF_3)_2C{=}C(OCH_3)_2$	−60	—
CH_3OCH_3	<−30	[7, 8]
CHF_2OCH_3	20	[8]
CHF_2OCHF_2	70	[8]
CF_3OCF_3	≫180	[8]

From Table 1 it can be seen that in the C_2F_4–C_3F_6–i-C_4F_8 series the ease of sulfotrioxidation decreases with increase in the electrophilicity of the olefin. The insertion of one, and even more so, of two methoxy groups sharply increases the nucleophilicity of the compounds and facilitates sulfotrioxidation. A coordinated shift of the p–π electron density occurs in the case of the monomethoxy derivative, with the fixation of a partial negative charge on the central C atom,

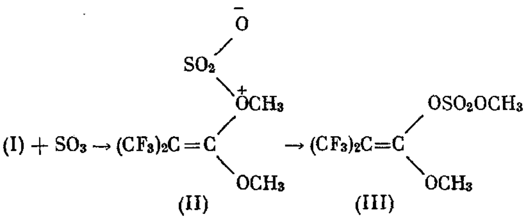


as a result of which the sulfotrioxidation of this compound takes place at the multiple bond and leads to the β-pyrosultone [6]

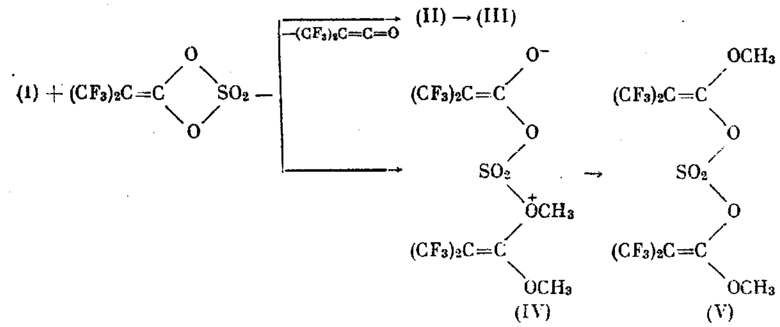


The possibility of the electron density of the ether oxygen shifting in this manner due to the induction effect is well illustrated by the conditions for the sulfotrioxidation of saturated ethers, where the reactivity is strongly dependent on the number of fluorine atoms in the molecule (see Table 1).

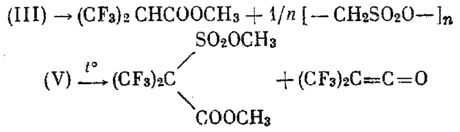
Of the compounds listed in Table 1, the bis(methoxy) olefin (I) is characterized by the highest nucleophilicity. However, the coupling of two CF_3 groups and two CH_3O groups in the (I) molecule leads to the oxygen atoms having a relatively greater electron-donor capacity than in the monomethoxy-substituted olefin. Consequently, (I) is sulfotrioxidated at the ether oxygen at a temperature (−60°) that is unusually low for fluoroolefins but is typical for ethers. Evidently, a bipolar ion of the oxonium type (II) is formed in the first step of the reaction, which is then stabilized by conversion to the unsymmetrical sulfate (III)



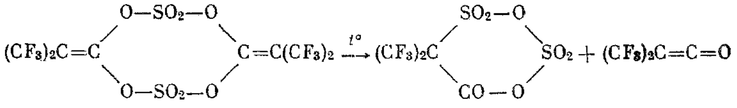
The reaction is more complicated in the case of hexafluoroisobutenylidene sulfate, which is capable of eliminating hexafluorodimethylketene [9], and this leads to the competing formation of two types of bipolar ions (II) and (IV), which are then stabilized by conversion to the two sulfates (III) and (V)



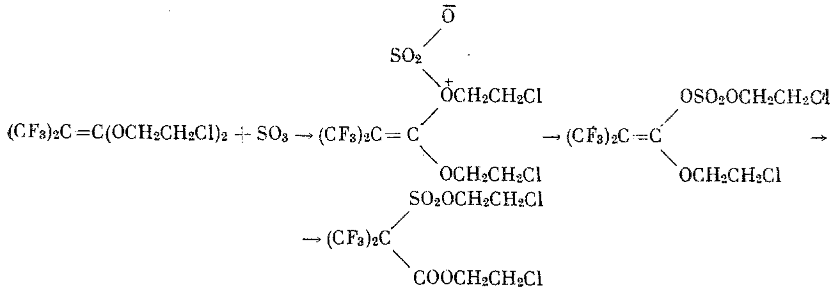
Sulfates (III) and (V), which are formed in the first reaction step, are unstable. The unsymmetrical sulfate (III) is probably decomposed by the intermolecular reaction scheme, and leads to the formation of methyl α-hydrohexafluoroisobutyrate and the α-polysultide. The symmetrical sulfate (V) is decomposed by heating, and here hexafluorodimethylketene is eliminated and the sulfonyl–carbon bond is generated



A precedent for the latter reaction is the known scheme for the decomposition of the hexafluoroisobutenylidene sulfate [10]



The previously described sulfotrioxidation of 1,1-bis-(β-chloroethoxy)hexafluoroisobutylene [1] must also be considered in a similar manner, which is also accomplished via the bipolar ion and leads to the intermediate sulfate, and then to the sulfonate



EXPERIMENTAL METHOD

1,1-bis(Methoxy)hexafluoroisobutylene (I). With stirring, 100 g of octafluoroisobutylene was condensed in a suspension of 54 g of CH_3ONa in 500 ml of anhydrous ether at −30°. The mixture was heated for 2 h at 15-20°, and the precipitate was filtered and washed with ether (4 × 50 ml). The mother liquor and extracts were combined. Fractional distillation gave 85.2 g (76%) of bisether (I) as a colorless liquid with bp 40° (10 mm); d_4^{20} 1.4310; n_D^{20} 1.3470; cf. [2].

Sulfotrioxidation. A. With stirring, to a solution of 11.2 g of bisether (I) in 60 ml of Freon-22 at −60° was added in 1 h, in drops, 4 g of freshly-distilled SO_3, stabilized with dimethyl sulfate (1%). Then the Freon was distilled off at −30°, the residue was heated to 0° and evacuated to 5-10 mm, and the distilled volatile products were condensed in a trap, cooled to −70°. The fractional distillation of the condensate gave 9.9 g (94%) of methyl α-hydrohexafluoroisobutyrate with bp 90°; d_4^{20} 1.4482; n_D^{20} 1.3081. Found: C 28.36; H 2.01%. $C_5H_4O_2F_6$. Calculated: C 28.57; H 1.91%. The compound was identified by GLC (comparison with a known specimen) and by the NMR spectrum (δ, ppm): 4.25 q (CH), J = 7.6 Hz, 3.89 s (CH_3) (relative to HMDS).

The remainder of the reaction mixture (4.7 g) is a white vaseline-like mass that is insoluble in water, benzene, CCl_4 or $CHCl_3$, is difficultly soluble in methanol, and is readily soluble in ether, acetone, or CH_3CN. When heated it dissolved in 5-10% caustic solutions; the hydrolyzate is inert toward oxidizing agents (I_2, $KMnO_4$) at pH 4-10.

B. With stirring and cooling with ice, to 11.2 g of bisether (I) was added in 1 h, in drops, 12.9 g of hexafluoroisobutenylidene sulfate. The mixture was heated in a dry nitrogen stream at 20-25°, and here the condensate, which was collected in a trap cooled to −70°, proved to be hexafluorodimethylketene, which was identified by GLC and ^{19}F NMR. Subsequent heating of the mixture on the water bath again resulted in the evolution of the ketene (a total of 8 g or 90%), while 5.3 g (50%) of methyl α-hydrohexafluoroisobutyrate was collected in the receiver. The fractional distillation of the mixture in vacuo gave 7.6 g (50%) of dimethyl α-sulfohexafluoroisobutyrate as a colorless liquid with bp 70° (10 mm); d_4^{20} 1.5010; n_D^{20} 1.3715. Found: C 23.81; H 2.10; F 37.19; S 10.32%. $C_6H_6O_5F_6S$. Calculated: C 23.67; H 1.97;

F 37.47; S 10.52%. NMR spectrum (δ, ppm): 3.59 s and 3.80 s. ^{19}F NMR spectrum: −14.6 s (relative to CF_3COOH). The residue presented 2.1 g of a white vaseline-like mass that was identical with that described above.

CONCLUSIONS

1. The reaction of 1,1-bis(methoxy)hexafluoroisobutylene with free and bound sulfur trioxide begins with attack of the ether oxygen.

2. The dimethyl ester of α-sulfohexafluoroisobutyric acid was obtained.

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