# FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

## III.* SULFOTRIOXIDATION OF α-HYDROHEXAFLUOROISOBUTYRIC ACID

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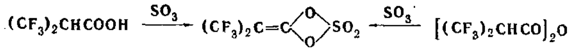
UDC 547.718'221

Depending on the conditions, α-hydrohexafluoroisobutyric anhydride, hexafluorodimethylketene, or hexafluoroisobutenylidene sulfate is formed in the sulfotrioxidation of α-hydrohexafluoroisobutyric acid. The sulfotrioxidation of α-hydrohexafluoroisobutyric anhydride similarly gives hexafluorodimethylketene or hexafluoroisobutenylidene sulfate.

It has previously been shown [2] that hexafluorodimethylketene reacts with sulfurtrioxide at 0°C to give hexafluoroisobutenylidene sulfate in quantitative yield. At the same time, it is known that hexafluorodimethylketene is formed when α-hydrohexafluoroisobutyric acid or its anhydride is heated with phosphorus pentoxide [3, 4]. In view of the dehydrating capacity of sulfur trioxide, it seemed possible to obtain hexafluoroisobutenylidene sulfate directly from α-hydrohexafluoroisobutyric acid or its anhydride on reaction with sulfuric anhydride.



It was found that the results of sulfotrioxidation are determined chiefly by the amount of sulfur trioxide used in the reactions.

α-Hydrohexafluoroisobutyric acid and sulfur trioxide react at 20° to give a 1:1 adduct. The adduct is relatively stable – neither ketene, sulfur trioxide, nor ketenal sulfate is isolated on evacuation, even at 100°. Only one doublet at δ –13.0 ppm, which is similar to the signal in the spectrum of the starting α-hydrohexafluoroisobutyric acid (δ –12.2 ppm), is observed in the $F^{19}$ NMR spectrum of the adduct.† When the adduct is heated above 150°, it undergoes decomposition accompanied by the isolation of hexafluorodimethylketene. The results of thermolysis change substantially in the presence of excess α-hydrohexafluoroisobutyric acid or sulfur trioxide. Thus if a 2:1 mixture of these reagents is used, thermolysis is also realized at 150° and gives α-hydrohexafluoroisobutyric anhydride. However, in the case of a 1:2 mixture, thermolysis (in a sealed glass ampul) begins at 80°, and hexafluoroisobutenylidene sulfate is formed. These facts make it possible to assert that the primary product in the sulfotrioxidation of α-hydrohexafluoroisobutyric acid is α-hydrohexafluoroisobutyrylsulfuric acid.

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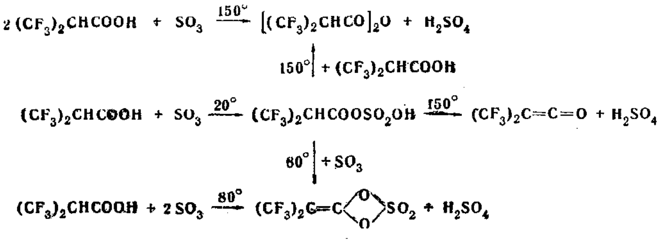
*See [1] for communication II.

†The $F^{19}$ NMR spectra were recorded with a Hitachi Perkin Elmer model R-20 spectrometer with a field strength of 14,092 G at 56.456 MHz. The chemical shifts (δ) were measured relative to trifluoroacetic acid (external standard).

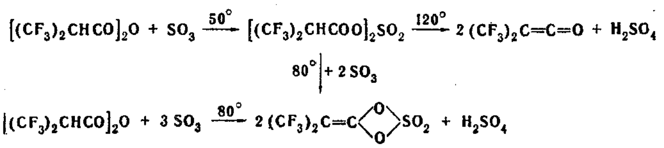
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 13-15, January, 1973. Original article submitted January 14, 1972.



By comparing the temperature conditions of the thermolytic processes under consideration, one can conclude that the formation of hexafluorodimethylketene during the dehydration of α-hydrohexafluoroisobutyric acid is not associated with the intermediate participation of its anhydride. On the contrary, it is more likely that the anhydride is the result of the final reaction of the ketene with excess acid. The possibility of this reaction was proved by direct experiment.

$$(CF_3)_2C{=}C{=}O + (CF_3)_2CHCOOH \xrightarrow{50^\circ} [(CF_3)_2CHCO]_2O$$

α-Hydrohexafluoroisobutyric anhydride reacts with sulfur trioxide only on heating above 50°, and a relatively stable 1:1 adduct is formed. At 120°, this adduct decomposes to give hexafluorodimethylketene. However, if α-hydrohexafluoroisobutryric anydride is heated with excess sulfur trioxide, decomposition commences at 80° and is accompaneid by the liberation of hexafluoroisobutenylidene sulfate. The yield of the latter is a maximum when the starting reagent ratio is 1:3. These observations make it possible to assume that the primary product of the sulfotrioxidation of α-hydrohexafluoroisobutyric anhydride is bis(α-hydrohexafluoroisobutyryl) sulfate.

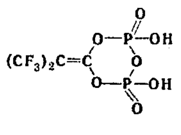


Thus, depending on the conditions, either hexafluorodimethylketene, hexafluoroisobutenylidene sulfate, or α-hydrohexafluoroisobutyric anhydride is formed in the sulfotrioxidation of α-hydrohexafluoroisobutyric acid; either the ketene or the ketenal sulfate is formed in the sulfotrioxidation of the latter. One cannot exclude the possibility that other products, for example,

$$(CF_3)_2C{=}C(OSO_2OH)_2$$

are formed in addition to the intermediate α-hydrohexafluoroisobutyrylsulfuric acid and bis(α-hydrohexafluoroisobutyryl) sulfate in the individual steps of the sulfotrioxidation.

In the light of the above, it can be assumed that the reaction of α-hydrohexafluoroisobutyric acid and its anhydride with phosphorous pentoxide is described in a more complex manner than was considered previously [3, 4]. It is known that both of these reactions are endothermic and that it is necessary to heat the reaction mixtures to 250° to obtain the ketene; in this case, one does not observe the liberation of the starting acid or anhydride, although they are quite volatile substances (bp 127 and 137°, respectively). It may be supposed that, as in sulfotrioxidation, intermediates of different types, for example,



are also formed in these cases.

## EXPERIMENTAL

α-Hydrohexafluoroisobutyric Anhydride. A. A 4.0-g (0.05 mole) sample of freshly distilled sulfur trioxide was added dropwise to 19.6 g (0.1 mole) of α-hydrohexafluoroisobutyric acid cooled to −20°, and the mixture was heated slowly initially to 20° (in the course of an hour) and then at 150° with a reflux condenser for 1-1.5 h. Subsequent double fractionation yielded 14.3 g (76%) of α-hydrohexafluoroisobutyric anhydride, which was identified from its physical properties and by $F^{19}$ NMR spectroscopy (δ −11.6 ppm; doublet) and alkalimetry [2].

B. A mixture of 8.9 g (0.05 mole) of hexafluorodimethylketene and 9.8 g (0.05 mole) of $\alpha$-hydrohexafluoroisobutyric acid was heated in a sealed glass ampul to 40-50°, during which the formation of a homogeneous mixture containing ketene, acid, and anhydride (according to $F^{19}$ NMR) was observed. The mixture was heated at 50° for 2 h, after which the ampul was cooled and broken open. The contents were fractionated to give 16.8 g (90%) of $\alpha$-hydrohexafluoroisobutyric anhydride.

Hexafluorodimethylketene. A. An 8.0 g (0.1 mole) sample of sulfur trioxide was added dropwise to 19.6 g (0.1 mole) of $\alpha$-hydrohexafluoroisobutyric acid cooled to −20°, and the mixture was heated to 20° and shaken periodically at this temperature for 1-1.5 h. During this treatment, we observed the formation of a homogeneous colorless liquid, the quantity and appearance of which remained unchanged on evacuation to a residual pressure of 10 mm and on heating to 100°. At 150°, the material underwent decomposition accompanied by the liberation of volatile substances, which were condensed in a trap cooled with ice–sodium chloride. Fractionation of the condensate gave 14.5 g (81%) of hexafluorodimethylketene, which was identified by gas-liquid chromatography (GLC), $F^{19}$ NMR spectroscopy ($\delta$ −22.0 ppm; singlet), and alkalimetry [2].

B. A 4.0 g (0.05 mole) sample of sulfur trioxide was added dropwise to 18.7 g (0.05 mole) of $\alpha$-hydrohexafluoroisobutyric anhydride at room temperature, and the mixture was heated with a reflex condenser at 50° until refluxing ceased (2-2.5 h). The temperature was then raised to 120°, and the resulting volatile decomposition products were condensed in a trap cooled with ice–salt mixture. Fractionation of the condensate gave 10.9 g of hexafluorodimethylketene.

Hexafluoroisobutenylidene Sulfate. A. A mixture of 9.8 g (0.05 mole) of $\alpha$-hydrohexafluoroisobutyric acid and 8.0 g (0.1 mole) of sulfur trioxide was sealed in a glass ampul and heated initially to 50° (with periodic shaking) and, after an hour, at 80° for 2-3 h. The ampul was then cooled to −78° and broken open, and the contents were fractionated to give 10.0 g (67%) of hexafluoroisobutenylidene sulfate, which was identified by GLC, $F^{19}$ NMR spectroscopy ($\delta$ −12.7 and −15.5 ppm; singlets), and alkalimetry [2].

B. A mixture of 18.7 g (0.05 mole) of $\alpha$-hydrohexafluoroisobutyric anhydride and 12.0 g (0.15 mole) of sulfur trioxide was sealed in a glass ampul and heated initially at 50° for 2 h and then at 80° for 2-3 h. The ampul was then cooled to −78° and broken open, and the contents were fractionated to give 13.7 g (53%) of hexafluoroisobutenylidene sulfate.

## LITERATURE CITED

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