FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

VI.* HEXAFLUOROTHIOACETONE DIOXIDE TRIMER

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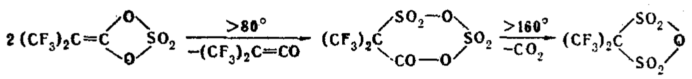
The reaction of bis(trifluoromethyl)ketene with bis(trifluoromethyl)methionic anhydride at 200°C has given hexafluorothioacetone dioxide trimer; 2,2,3,3-tetrakis(trifluoromethyl)-thiirane 1,1-dioxide is formed as a byproduct. The same trimer is obtained by heating hexafluoroisobutenylidene sulfate and by treating hexafluoro-αH-isobutyric acid with sulfur trioxide.

It has been shown previously [1] that hexafluoroisobutenylidene sulfate (I) undergoes intramolecular sulfonation on being heated above its boiling point (~49°C) with the liberation of bis(trifluoromethyl)ketene (II); the internal anhydride of hexafluoro-α-pyrosulfonylisobutyric acid (III) formed in this process decarboxylates and is converted into bis(trifluoromethyl)methionic anhydride (IV). On the basis of these facts, it appeared that the anhydride (IV) could be obtained directly from compound (I) by heating above 160°C.



I II III IV

However, it proved impossible to isolate the anhydride (IV) and the ketene (II) from the products of the pyrolysis of the ketene sulfate (I). Furthermore, these compounds are incompatible in pyrolytic processes.

The first indications of the reaction of the anhydride (IV) with bis(trifluoromethyl)ketene (II) were observed at temperatures as low as 50-60°C (coloration of the reaction mixture); at 120-130°C, the reaction became exothermic; when the mixture was heated above 180°C, a vigorous evolution of carbon dioxide and of sulfur dioxide took place. If the process was completed by heating the mixture to 200°C, it was possible to isolate the liquid 2,2,3,3-tetrakis(trifluoromethyl)thiirane 1,1-dioxide (V) (15%) and the crystalline hexafluorothioacetone dioxide trimer (VI) (75%). The formation of these compounds can be explained only by the intermediate participation in the reaction of the monomeric hexafluorothioacetone dioxide (VII).

Apparently, in the first stage the acylation of the ketene (II) by the anhydride (IV) with the formation (at 50-60°C) of the ketene methionate (VIII), intramolecular sulfonation in the latter (at 120°C and above), and decarboxylation (at 180-200°C) take place successively. The symmetrical cyclic disulfone (IX) formed dissociates under the reaction conditions into the monomeric hexafluorothioacetone dioxide (VII); it is possible that this is an equilibrium process. The thioacetone dioxide (VII) is unstable and tends either to evolve sulfur dioxide with the formation of the thiirane dioxide (V) or to undergo association to form the six-membered cyclic trimer (VI).

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*For Communication V, see [1].

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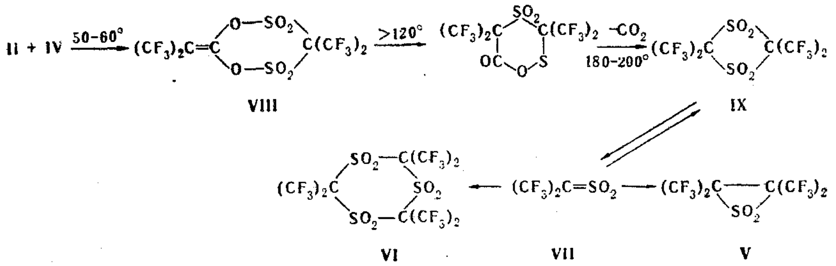


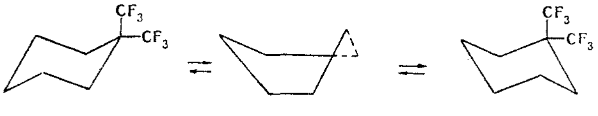
The correctness of the considerations put forward follows from the general laws of the chemistry of the thioketene dioxides [2] and from the known characteristics of transformations among hexafluorothioacetone derivatives [3, 4]. The thermal stability of the thioacetone dioxide trimer (VI) formed at 200°C is not surprising, since examples are known of stable cyclic compounds with an alternating arrangement of pairs of trifluoromethyl substituents [3, 4].

The structure of the thiirane dioxide (V) was confirmed by the ^{19}F NMR method and by the results of alkaline hydrolysis, which took place in accordance with the following equation:

$$V+9\bar{O}H \rightarrow CH_3C(CF_3)_2SO_2\bar{O}+2HC\bar{O}_3+6\bar{F}+2H_2O.$$

The trimeric composition of compound (VI) was shown by a molecular-weight determination (cryoscopy in Freon-113). The presence of trifluoromethyl and sulfonyl groups was shown by IR spectroscopy. The sharp values of the observed frequencies of the stretching vibrations show the monotypicity of all six CF_3 groups and of all three sulfonyl groups. This is evidence in favor of the spatial symmetry of the molecule of the trisulfone (VI). Since the trisulfone (VI) is a derivative of 1,3,5-trithiane, on the basis of the general laws of conformational analysis [5], the chair-shaped conformation is the best-justified for it.

The ^{19}F NMR spectrum of compound (VI) (melt, and also solutions in dimethyl sulfate or in sulfuryl chloride) contains only one singlet signal, which shows that under the conditions of the experiment the molecule of (VI) exists in the form of a single conformation in which the sulfur atoms of the ring are present on one side of the chiral plane and the carbon atoms of the ring on the other side. Probably, in the melt (above 83°C) or in solution (at 34.5°C) there is a rapid conformational conversion of the chair structure into its antipode, when all the axially arranged trifluoromethyl groups change into the equatorial positions, and conversely.



The singlet nature of the signal in the ^{19}F NMR spectrum reflects some averaging of the positions of the trifluoromethyl groups (50% a and 50% e) and shows that the potential barrier to inversion is low. We have observed some differences in the IR spectra of crystalline and dissolved samples (see [5]) which permits the assumption that inversion takes place through a stage of a distorted "boat-shaped" form.

In spite of its extremely complex composition, compound (VI) readily distills (bp 128-129°C), and it sublimes more readily than naphthalene and adamantane. Sublimation takes place even at atmospheric pressure (20-25°C) and proceeds extremely rapidly at a residual pressure of 50-60 mm. If sublimation is performed in a closed space at a temperature drop of 20-30°C, it is possible to grow a single crystal of the trimer (VI) resembling mother of pearl and with a size of 3-4 mm; the shape of the crystal is polyhedral with the form of a flattened crown having a third-order axis of symmetry.

The trimer (VI) can also be obtained with a yield of 70% by the pyrolysis of hexafluoroisobutenylidene sulfate (I) or directly (with the yield of 52%) by treating hexafluoro-αH-isobutyric acid with sulfur trioxide.

$$3(CF_3)_2CHCOOH+6SO_3 \rightarrow VI \xleftarrow[-CO_2]{} 3I$$

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Hitachi–Perkin–Elmer model R-20 instrument (56.456 MHz). The chemical shifts (δ) were measured in parts per million of the field relative to trifluoroacetic acid (external standard). The IR spectra were obtained on a IKS-12 spectrograph.

Hexafluorothioacetone Dioxide Trimer (VI). A. A mixture of 14.7 g (0.05 mole) of the anhydride (IV) and 8.9 g (0.05 mole) of the ketene (II) was heated in a steel autoclave first at 120°C for 2 h and then at 200°C for 2 h. After cooling, the reaction mixture was filtered through a glass filter. The filtrate (4.2 g) was washed with water, dried with magnesium sulfate, and fractionally distilled. This gave 2.7 g (15%) of 2,2,3,3-tetrakis(trifluoromethyl)thiirane 1,1-dioxide (V) in the form of a colorless liquid with bp 84°C, d_4^{20} 1.7330, n_D^{20} 1.3155. ^{19}F NMR spectrum (20% solution in CCl_4): singlet with δ −17.0 ppm. Found %: C 19.4; F 62.0; S 9.0. $C_6F_{12}O_2S$. Calculated %: C 19.8; F 62.4; S 8.8. On alkaline hydrolysis (0.1 N KOH), the consumption of alkali was 9.1 equivalents in the presence of phenolphthalein and 6.9 equivalents in the presence of Methyl Orange; 5.94 equivalents of fluoride ion was found in the hydrolyzate.

The precipitate (17.1 g) was washed with water and was mixed with magnesium sulfate, and the mixture was sublimed at 100–130 mm (in the water bath); this gave 16.0 g (75%) of the hexafluorothioacetone dioxide trimer (VI) in the form of colorless prismatic crystals with mp 83°C and bp 128–129°C. ^{19}F NMR spectrum (melt at 85–90°C or 20% solutions in dimethyl sulfoxide or sulfuryl chloride at 34.5°C): singlet with δ −18.3 ppm. IR spectrum: thin layer of a mull in paraffin oil — 1130 and 1472 cm^{-1} (sulfonyl group), 1270 cm^{-1} (trifluoromethyl group); in CCl_4 — broad absorption bands at 1128–1135, 1265–1280, and 1470–1478 cm^{-1}. Found %: C 16.6; F 53.8; S 15.0; mol. wt. (cryoscopically in Freon-113) 624. $C_9F_{18}O_6S_3$. Calculated %: C 16.8; F 53.5; S 15.0; mol. wt. 642. The substance is readily soluble in dimethyl sulfate and sulfuryl chloride, fairly soluble (about 10%) in alcohols, ethers, and dioxane; sparingly soluble (about 5%) in benzene and carbon tetrachloride; slightly soluble in carbon sulfide; and insoluble in water.

B. Under the conditions given above, 25.8 g of hexafluoroisobutenylidene sulfate yielded 1.8 g (10%) of the thiirane dioxide (V) and 15.0 g (70%) of the trimer (VI).

C. A mixture of 19.6 g (0.01 mole) of hexafluoro-αH-isobutyric acid and 16.0 g (0.02 mole) of freshly-distilled sulfur trioxide was heated in a steel autoclave at 200°C for 8 h. The reaction mixture was filtered, and the precipitate was washed with water and was mixed with magnesium sulfate. Sublimation yielded 11.0 g (52%) of hexafluorothioacetone dioxide trimer.

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