FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

VIII.* TRANSFORMATIONS OF HEXAFLUORODIMETHYL SULFONENE TRIMER UNDER BASE SOLVOLYSIS CONDITIONS

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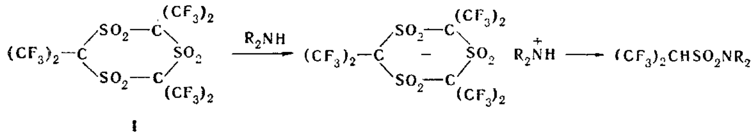
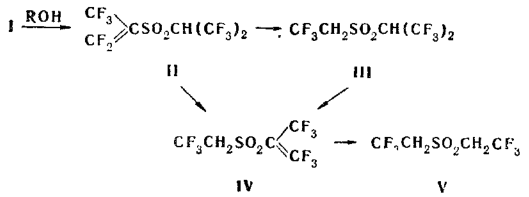
Salts of hexafluorodimethylmethionic and α-hydrohexafluoro-2-propane-2-sulfonic acids, the amide of the latter, and a number of sulfones containing α-hydrohexafluoroisopropyl, pentafluoroisopropenyl, β,β,β-trifluoroethyl, and methyl groups were obtained by alkaline hydrolysis, alcoholysis, and ammonolysis of hexafluorodimethyl sulfonene trimer.

In a preceding communication it was shown that cyclic trisulfone I, which is a trimer of hexafluorodimethyl sulfonene, reacts with nucleophilic reagents to give donor-acceptor complexes; complexes based on secondary amines are unstable – they decompose to give amides of α-hydrohexafluoropropane-2-sulfonic acid [1]. In the present communication,



we examine the transformations of trisulfone I during alcoholysis, alkaline hydrolysis, and ammonolysis.

It was found that solutions of trisulfone I in methanol, ethanol, and benzyl and other alcohols are stable at 20°C for many weeks (according to monitoring by UV and ^{19}F NMR spectroscopy). Reaction between trisulfone I and aliphatic alochols occurs only when the mixture is heated above 60-70°; in this case, different products are formed, depending on the reagent ratio. Thus, when a limited amount (the optimum is 2-3 equivalents) of alcohol is used, α-hydrohexafluoroisopropyl pentafluoroisopropenyl sulfone (II) can be isolated; β,β,β-trifluoroethyl α-hydrohexafluoroisopropyl sulfone (III) is isolated in the case of excess alcohol (6 or more equivalents). Sulfone II can be converted to sulfone III by treatment with alcohol or water. Both sulfones are stable on storage in sealed quartz ampoules but are unstable when they are stored in ordinary laboratory (alkali) glass; when they are stored in ordinary laboratory glass, each of these sulfones is



converted to β,β,β-trifluoroethyl pentafluoroisopropenyl sulfone (IV) (after 2-2.5 weeks and 8-10 months, respectively). Treatment of IV with alcohol or water gives the extremely stable bis(β,β,β-trifluoroethyl) sulfone (V).

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[*] See [1] for communication VII.

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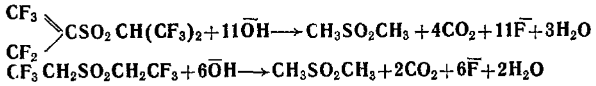
The structures of all of these fluorine-containing sulfones were proved by ^{19}F NMR spectroscopy and from the results of alkalimetry and thoriometry, for example:



$$\overset{CF_3}{\underset{CF_2}{}}\!\!>\!CSO_2CH(CF_3)_2+11\bar{O}H \longrightarrow CH_3SO_2CH_3+4CO_2+11\bar{F}+3H_2O$$

$$CF_3CH_2SO_2CH_2CF_3+6\bar{O}H \longrightarrow CH_3SO_2CH_3+2CO_2+6\bar{F}+2H_2O$$

A strict sequence of formation of the reaction products is also observed during the alkaline hydrolysis of trisulfone I. In this case, a rapid reaction is realized at 20°; the result of the reaction depends on the amount of alkali used. Thus, if two equivalents of potassium hydroxide in alcohol are used in the treatment of solutions of trisulfone I (in dioxane or alcohol), a hexafluorodimethylmethionic acid salt (VI) is formed, while three equivalents of alkali give an α-hydrohexafluoropropane-2-sulfonic acid salt (VII), which can also be obtained directly from salt VI. If trisulfone I is treated with aqueous alkalis, one can isolate fluorine-containing sulfones that are identical to those described above – III (optimally six equivalents of alkali) and V (optimally 9-12 equivalent of KOH). Dimethyl sulfone (18 or more equivalents of KOH) and a sulfoacetic acid salt (22 or more equivalents of KOH) are formed when excess alkali is used. It was established by analytical experiments that these latter compounds along with carbon-dioxide gas and salts of sulfuric and hydrofluoric acids, are the final products of the alkaline hydrolysis of trisulfone I; the overall consumption of alkali is 22 equivalents with respect to methyl orange or 27 equivalents with respect to phenolphthalein.

On the basis of the experimental facts presented above, it can be asserted that the alkaline hydrolysis of trisulfone I is a multistep process and is characterized by a strictly determined sequence of steps that is determined by the stabilities of the products formed.

$$\mathrm{I}+2KOH \longrightarrow \mathrm{II}+\underset{\mathrm{VI}}{KOSO_2C(CF_3)_2SO_2OK}+HF$$

$$\mathrm{I}+3KOH \longrightarrow \mathrm{II}+\underset{\mathrm{VII}}{(CF_3)_2CHSO_2OK}+K_2SO_4+HF$$

$$\mathrm{I}+6KOH \longrightarrow \mathrm{III}+\mathrm{VII}+K_2SO_4+3KF+CO_2+H_2O$$

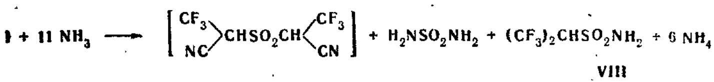
$$\mathrm{I}+9KOH \longrightarrow \mathrm{V}+\mathrm{VII}+K_2SO_4+6KF+2CO_2+2H_2O$$

$$\mathrm{I}+12KOH \longrightarrow \mathrm{V}+CF_3CH_2SO_2OK+K_2SO_4+9KF+3CO_2+3H_2O$$

$$\mathrm{I}+18KOH \longrightarrow CH_3SO_2CH_3+CF_3CH_2SO_2OK+K_2SO_4+15KF+5CO_2+5H_2O$$

$$\mathrm{I}+22KOH \longrightarrow CH_3SO_2CH_3+KOOCCH_2SO_2OK+K_2SO_4+18KF+5CO_2+7H_2O$$

The alcoholysis of trisulfone I is realized via a similar scheme. It might be assumed that the amides of α-hydrohexafluoropropane-2-sulfonic acid, which were previously obtained in the reaction of trisulfone I with secondary amines [1], are formed via a similar scheme. The result of the ammonolysis of trisulfone I is an additional confirmation of this. Thus, its reaction with ammonia in benzene solution is accomplished at 20°, during which the ammonia consumption is ~11 equivalents; sulfamide and α-hydrohexafluoropropane-2-sulfamide (VIII) were isolated from the reaction products; ammonium fluoride (six equivalents) is formed simultaneously.

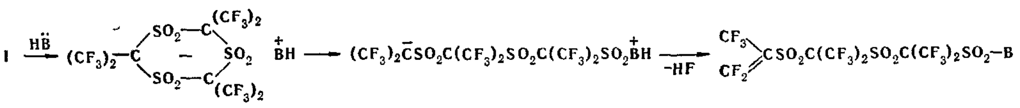


$$\mathrm{I}+11\,NH_3 \longrightarrow \left[\overset{CF_3}{\underset{NC}{}}\!\!>\!CHSO_2CH\!<\!\overset{CF_3}{\underset{CN}{}}\right]+H_2NSO_2NH_2+\underset{\mathrm{VIII}}{(CF_3)_2CHSO_2NH_2}+6\,NH_4F$$

The α-hydrohexafluoropropane-2-sulfamide structure was proved by ^{19}F NMR spectroscopy and also from the results of alkalimetry and thoriometry. Bis(α-cyano-β,β,β-trifluoroethyl) sulfone could not be isolated; its formation can only be postulated on the basis of the stoichiometry of the reaction under consideration and in analogy with the results of the ammonolysis of hexafluoropropylene [2].

$$CF_3CF{=}CF_2 \xrightarrow{NH_3} [CF_3CHFCF_2NH_2] \xrightarrow[-HF]{} CF_3CHFCN$$

One's attention is drawn to the fact that sulfonyl-containing compounds of three types – sulfones, sulfuric acid, and sulfonic acid derivatives – are always formed in the exhaustive alcoholysis, hydrolysis, or ammonolysis of trisulfone I. When the process was controlled (2 equivalents of KOH), in place of the latter acid derivatives, we were able to record a hexafluorodimethylmethionic acid derivative (VI). The precursor of all of these substances is apparently a trisulfonyl compound that is formed in the first steps of the process – coordination of the nucleophile (of the H–B) type with trisulfone I, decyclization of the latter under the solvolysis conditions to a dipolar ion of the linear type, and stabilization of this ion by splitting out of a fluoride ion.



This interpretation of the first steps of the above-examined transformations of trisulfone I clearly explains the results of alcoholysis, alkaline hydrolysis, ammonolysis, and aminolysis. This makes it possible to predict that the reaction of cyclic trisulfone I with all nucleophilic reagents will be realized via the same scheme presented above.

EXPERIMENTAL

The ^{19}F NMR spectra were recorded by I. V. Galakhov and L. I. Ragulin with a Hitachi – Perkin Elmer model R-20 spectrometer at 34.5°; the field intensity was 14,092 G, the frequency was 56.456 MHz, the resolution was $3 \cdot 10^{-8}$, and the external standard was trifluoroacetic acid. The spectral data are presented in Table 1.

Hexafluorodimethyl Sulfonene Trimer (I). This compound was obtained by pyrolysis of hexafluoroisobutenylidene sulfate [3] and was purified by sublimation.

α-Hydrohexafluoroisopropyl Pentafluoroisopropenyl Sulfone (II). A 3.24-g (0.03 mole) sample of benzyl alcohol was added to a solution of 6.42 g (0.01 mole) of I in 50 ml of dioxane, and the mixture was heated on a boiling-water bath for 3 h. The solvent was then removed by vacuum distillation, and the residue was mixed with anhydrous magnesium sulfate; the mixture was placed in a sublimation apparatus (of the finger type), and the sublimate was collected by heating on a water bath (at 50-80 mm). This procedure gave 2.4 g (69%) of sulfone II as white plates with mp 33°. Found: C 21.0; H 0.5; F 60.0; S 9.5%. $C_6HO_2F_{11}S$. Calculated: C 20.8; H 0.3; F 60.4; S 9.3%.

Similarly, 2.1 g (60%) of II was obtained from 6.42 g of I and 1.84 g of ethanol.

β,β,β-Trifluoroethyl α-hydrohexafluoroisopropyl Sulfone (III). A solution of 6.42 g (0.01 mole) of I in 30 ml of methanol was heated at 70° for 1 h, during which a crystalline precipitate formed. The mixture was cooled, and the precipitate was removed by filtration and sublimed from a mixture with magnesium sulfate to give 2.5 g (84%) of sulfone III as white needles with mp 55°. Found: C 20.0; H 1.1; F 57.1; S 11.1% $C_5H_3O_2F_9S$. Calculated: C 20.1; H 1.0; F 57.4; S 11.7%.

Similarly, III was obtained in 78% yield by heating a solution of I in benzyl alcohol at 100°.

A methanol solution of 3.66 g (~0.05 mole) of potassium hydroxide was added slowly to a solution of 6.42 g (0.01 mole) of I in 150 ml of methanol, during which a precipitate formed. The solvent was removed by vacuum distillation, and the residue was extracted twice with hot dibutyl ether in 10-ml portions. Cooling of the extract to 0° gave 2.7 g (90%) of III.

A 0.5-ml sample of water or ethanol was added to a solution of 1.7 g (0.005 mole) of sulfone II in hot dibutyl ether, and the mixture was cooled to 0° to give 1.4 g (94%) of sulfone III.

β,β,β-Trifluoroethyl Pentafluoroisopropenyl Sulfone (IV). Crystalline sulfone II was stored in a sealed glass ampoule at 20 ± 3° for 18 days. The crystalline mass was then mixed with magnesium sulfate and sublimed to give sulfone IV (76%) as white prisms with mp 129°. Found: C 21.2; H 1.0; F 54.5; S 12.0%. $C_5H_2O_2F_8S$. Calculated: C 21.6; H 0.7; F 54.7; S 11.5%.

Crystalline sulfone III was stored in a sealed glass ampoule at 20 ± 5° for 280 days. Sublimation of a mixture of this material with magnesium sulfate gave sulfone IV in 64% yield.

Bis(β,β,β-trifluoroethyl)sulfone (V). An alcohol solution of 4.94 g (0.09 mole) of potassium hydroxide was added slowly to a solution of 6.42 g (0.01 mole) of I in 150 ml of ethanol, during which a precipitate formed. The solvent was removed by vacuum distillation, and the residue was extracted twice with 10-ml portions of hot dioxane. Cooling of the extract to 20° gave 2.0 g (87%) of sulfone V as white scales with mp 127°. Found: C 21.1; H 2.1; F 49.3; S 14.3%. $C_4H_4O_2F_6S$. Calculated: C 20.8; H 1.7; F 49.6; S 13.9%.

A 0.5-ml sample of water or ethanol was added to a solution of 1.4 g (0.005 mole) of sulfone IV in hot dioxane, and the mixture was cooled to 20° to give 1.1 g (95%) of sulfone V.

Potassium Hexafluorodimethylmethionate (VI). A solution of 1.12 g (0.02 mole of potassium hydroxide in 10 ml of methanol was added to a solution of 6.42 g (0.01 mole) of I in 100 ml of methanol, during which a precipitate formed. The solvent was removed by vacuum distillation at room temperature, and the residue was washed with 10 ml of hot dioxane to give 3.5 (90%) of salt VI as white scales with mp 189° (decomp. pt.). Found: C 8.9; F 28.9; S 16.1%. $C_3O_6F_6S_2K_2$. Calculated: C 9.3; F 29.4; S 16.5%. Salt VI was soluble in water (with decomposition) and insoluble in most organic solvents.

TABLE 1

Compound	Alkalimetry			^{19}F NMR spectra			
	KOH consump., equiv.		fluoride ion found, equiv.	solvent	signal character	chemical shift, ppm	spin–spin coupling constant
	phenolphthalein	Methyl Orange					
I	26,91	22,12	18,01	Dioxane	Singlet	−18,3	—
II	15,10	11,15	11,05	Dioxane	Multiplet, doublet, multiplet	−23,0 −16,3 −4,0	— 8,1 —
III	11,93	8,94	9,10	Dioxane	Doublet, triplet	−16,2 −17,0	8,0 9,0
IV	10,93	8,03	7,98	Dioxane	Multiplet, triplet, multiplet	−23,0 −16,7 −4,0	— 9,0 —
V	8,05	5,99	5,94	Dioxane	Triplet	−16,0	9,0
VI	8,97	7,95	5,91			—	—
VII	7,94	6,98	5,93	Water	Doublet	−15,8	8,0
VIII	7,95	6,93	5,91	Alcohol	Doublet	−16,2	9,0

Potassium α-Hydrohexafluoropropane-2-sulfonate (VII). A solution of 1.68 h (0.03 mole) of potassium hydroxide in 10 ml of methanol was added dropwise to a solution of 6.42 g (0.01 mole) of I in 25 ml of dioxane, during which a precipitate formed. The precipitate was removed by filtration and recrystallized from 50% aqueous ethanol to give 2.0 g (74%) of salt VII as white prisms with mp 254° (decomp. pt.). Found: C 13.0; H 0.6; F 42.0; S 12.3%. $C_3HO_3F_6SK$. Calculated: C 13.3; H 0.4; F 42.4; S 11.8%.

Recrystallization of salt VI from water–ethanol (1 : 1) gave salt VII in 94% yield.

Alkaline Hydrolysis of Trisulfone I. A suspension of 32.8 g (~0.1 mole) of barium oxide octahydrate in 100 ml of water was added to a solution of 6.42 g (0.01 mole) of I in 100 ml of ethanol, and the mixture was shaken vigorously for 2 h. The precipitate was centrifuged, removed by filtration, and washed with 10 ml of hydrochloric acid (1 : 5) and 10 ml of water. It was then transferred to a 100-ml volumetric flask, and sulfuric acid (1 : 10) was added up to the mark. The fluoride ion content (17.6 equivalents) in an aliquot of this solution was determined.

The mother liquor was evaporated, and the residue was washed twice with 10-ml portions of ether and recrystallized from aqueous alcohol (1 : 1) to give 2.5 g (91%) of barium sulfoacetate. Found: C 8.7; H 0.8; S 11.6%. $C_2H_2O_5SBa$. Calculated: C 8.9; H 0.7; S 11.8%.

The ether extract was evaporated, and the residue was recrystallized from toluene to give 0.8 g (85%) of dimethyl sulfone, which was identical to a genuine sample.

α-Hydrohexafluoropropane-2-sulfamide (VIII). Dry ammonia was bubbled slowly into a solution of 4.6 g (0.007 mole) of I in 150 ml of dry benzene until the signs of a reaction – heat evolution and formation of a white precipitate – ceased. The ammonia consumption was 1.8–1.9 liter. The benzene was removed from the reaction mixture by vacuum distillation, and the residue was extracted twice with 15-ml portions of hot chloroform. The extract was cooled to 0° to give 1.6 g (97%) of sulfamide VIII as white scales with mp 103.5°. Found: C 15.2; H 1.2; N 5.8; F 49.2; S 13.7%. $C_3H_3O_2NF_6S$. Calculated: C 15.6; H 1.3; N 6.1; F 49.4; S 13.8%.

The residue from the reaction mixture was treated with water, and the fluoride ion content (6.08 equivalents) in an aliquot was determined.

Alkalimetry. A weighed sample (0.01–0.03 g) of the test preparation was dissolved in 10 ml of ethanol, and the solution was diluted with 50 ml of 0.1 N potassium hydroxide. After 24 h, the excess alkali was titrated with 0.1 N hydrochloride, first with respect to phenolphthalein and then with respect to Methyl Orange. In other experiments the fluoride ion content in the alkaline hydrolyzate was determined by thoriometry. The results of the analyses are presented in Table 1.

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