FLUOROALIPHATIC ESTERS OF FLUOROSULFONIC ACID. 4. REACTIONS OF α-FLUOROSULFATOPERFLUORO KETONES WITH NUCLEOPHILIC REAGENTS

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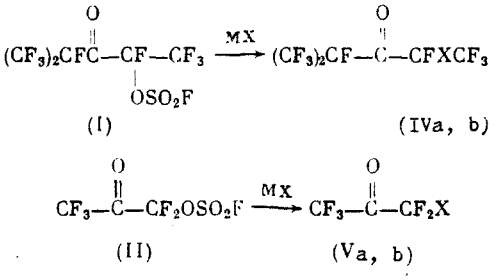
α-Fluorosulfatoperfluoroethyl isopropyl ketone I and fluorosulfatopentafluoroacetone II react with alkali metal chlorides and bromides to form the corresponding α-haloperfluoro ketones as a result of direct nucleophilic substitution.

Nucleophilic substitution reactions which result in the replacement of an FSO_3 group by a nucleophile are not characteristic of 1-fluorosulfatoperfluoroalkanes, since the attack of the nucleophile is directed at the S atom [1]. At the same time, "soft" nucleophiles react smoothly with esters of fluorosulfatodifluoroacetic acid, i.e., compounds containing a carbonyl group in the α position to the FSO_3 group, and replace the FSO_3 group in S_N2 reactions [2]. The structural similarity of perfluorinated α-keto fluorosulfates (PFK's) to alkyl fluorosulfatodifluoroacetates suggested that these compounds will also undergo direct nucleophilic replacement of the FSO_3 group. However, the examples of reactions of PFK's with nucleophiles described in the literature did not confirm this hypothesis. For example, although the reaction of I with CsF produces perfluoroethyl isopropyl ketone III, it takes place in two steps with the intermediate formation of 2-trifluoromethylperfluoro-2-pentane oxide, i.e., the replacement of the FSO_3 group is realized according to an S_Ni mechanism [3], and ketone II isomerizes under the action of NaI to α-fluorosulfatotetrafluoropropionyl fluoride [4]. Thus, the question of the possibility of the direct nucleophilic replacement of the FSO_3 group in a PFK is still open.

In the present work we studied the reactions of I and II with halide anions and some O and S nucleophiles. For example, compounds I and II react with LiCl and KBr, giving the corresponding α-halo ketones:



M = Li, K; X = Cl (a); X = Br (b).

It might have been postulated that, like ketone III, halo ketones IVa and b are also formed as a result of the opening of the ring in the intermediately produced α oxide. However, the formation of a mixture of isomeric α-chloro ketones IVa and VIII when a mixture of the keto fluorosulfates is reacted with LiCL refutes this hypothesis, since in the case of the intermediate formation of α-oxide VII, the products of the opening of the ring in it by a Cl^- anion should include α,α-dichloro ketone IX, whose presence, however, was not detected.

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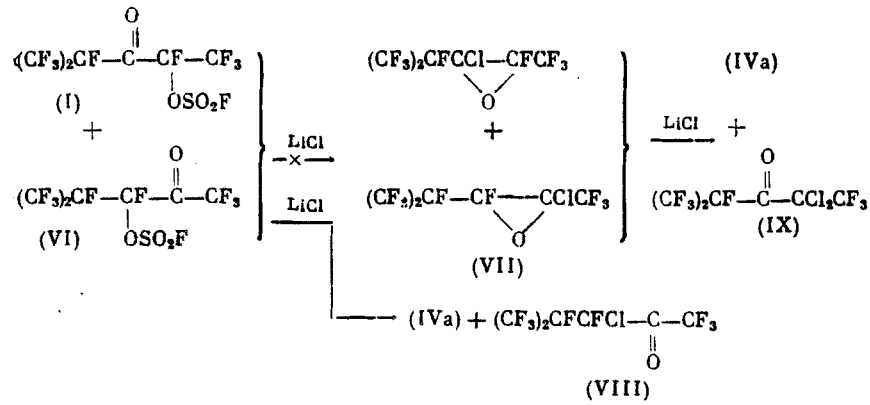
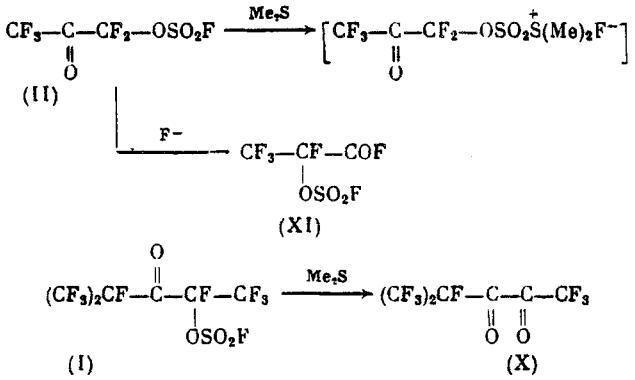
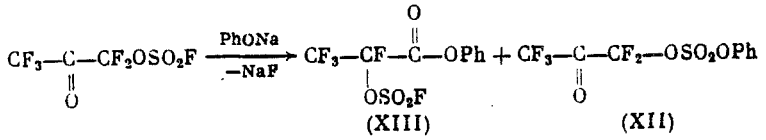


Thus, it may be concluded that α-halo ketones IVa and b form as a result of the direct nucleophilic replacement of the fluorosulfato group in I by a halogen atom. The synthesis of ketones Va and b takes place in the same way, and the intermediate formation of hexafluoropropylene oxide should be ruled out, since the opening of the ring in this compound by halide anions should produce α-halotetrafluoropropionyl fluorides, rather than Va and b.

It was not possible to replace the FSO_3 group by an MeS group by reacting I with Me_2S: when the mixture of reactants was heated to 60°C, the conversion of I was not observed, and the only reaction product obtained at 90°C was 2-trifluoromethylperfluoropenta-2,3-dione X. Apparently, when the temperature is raised, dimethyl sulfide attacks I at the S atom, generating an F^- anion, which causes I to split at the O–S bond. The generation of F^- can also account for the isomerization of II to α-fluorosulfatotetrafluoropropionyl fluoride XI in the reaction of II with Me_2S:



The reaction of II with PhONa unexpectedly resulted in the formation of a mixture of pentafluoroacetonyl phenyl sulfate XII and phenyl α-fluorosulfatotetrafluoropropionate XIII. The formation of the latter is definitely associated with the isomerization of II under the action of the NaF released.



It is difficult to explain the preferential formation of sulfate XII and the absence of phenoxypentafluoroacetone, i.e., the product of the replacement of the FSO_3 group in II by a PhO group, and products of the splitting of II at the O—S bond. It should, however, be noted that a similar reaction was previously observed when 4-chloroperfluorohexa-2,5-dienyl fluorophosphate was reacted with MeOH at reduced temperatures [5].

EXPERIMENTAL

The ^{19}F NMR spectra were recorded on a Perkin—Elmer R-32 spectrometer (84.6 MHz) and a Bruker WP-200 SY spectrometer (188.3 MHz). The chemical shifts are given in ppm relative to CF_3COOH (an external reference). The

mass spectra were recorded on a VGMS 70-70E spectrometer with an ionizing voltage corresponding to 70 eV; *m/z*, the intensity in percent in parenthesis, and the proposed assigned are presented.

Reaction of α-Fluorosulfatotetrafluoroethyl Heptafluoroisopropyl Ketone (I) with Alkali Metal Halides (typical procedure). A. A mixture of 1.8 g of dry LiCl and 15 ml of absolute diglyme was given a dropwise addition of 10 g of keto fluorosulfate I with stirring (20°C). The reaction mixture was stirred for 2 h at 20°C, and then the lower layer was separated. The reaction mass was poured into water, and the organic layer was combined with the layer separated in the preceding step and distilled over concentrated H_2SO_4. This gave 6.7 g of a fraction with a bp up to 30°C (40 mm Hg) containing (GLC, ^{19}F NMR) 4.4% keto fluorosulfate I, 63.6% ketone IVa [6], and 31.9% diketone X [7].

The reaction of 2.4 g of LiBr and 6.9 g of keto fluorosulfate I in 15 ml of diglyme as in procedure A (10°C, 3 h) gave 4.1 g of a mixture containing (GLC, ^{19}F NMR) 11% diketone X and 89% ketone IVb with bp 94°C. Found: C, 18.96; F, 55.49 Br, 21.15%. Calculated for $C_6F_{11}BrO$: C, 19.10; F, 55.44; Br, 21.22%. ^{19}F NMR spectrum (δ, ppm): —4.1 br. s $(CF_3)_2$, —0.2 br. s (CF_3), 68.5 br. d (CFBr), 108 br. d (CF, $J_{CF-CFBr}$ = 47 Hz).

The reaction of 3.5 g of NaI and 7.9 g of keto fluorosulfate I in 15 ml of diglyme as in procedure A (10°C, 3 h) gave 4.8 g (83%) of ketone X (GLC, ^{19}F NMR) [7].

Reaction of Fluorosulfatopentafluoroacetone (II) with Alkali Metal Halides. The reaction of 4.5 g of keto fluorosulfate II with 1 g of LiCl in 15 ml of diglyme was carried out in analogy to procedure A (25°C, 30 min), and the reaction products were distilled from the reaction mass at 20°C (50 mm Hg) with collection of the low-boiling fraction in a trap (—78°C). Subsequent distillation gave 2.9 g (88%) of ketone Va with bp 10°C (GLC, ^{19}F NMR) [8].

The reaction of 3 g of LiBr and 7 g of keto fluorosulfate I in 15 ml of diglyme (25°C, 1 h) as in procedure A gave 5.2 g (80%) of ketone Vb with bp 31-33°C (GLC, ^{19}F NMR) [8].

Reaction of Keto Fluorosulfates (I) and (VI) with LiCl. The reaction of 3 g of a mixture of keto fluorosulfates I and VI with 0.5 g of LiCl in 15 ml of diglyme was carried out in analogy to procedure A (10°C, 1 h), and then distillation of the organic layer over concentrated H_2SO_4 gave 1.7 g of a fraction with a bp up to 30°C (40 mm Hg) containing (GLC, ^{19}F NMR) 76.6% IVa, 5.8% VIII [6], and 17.6% VI.

Reaction of α-Fluorosulfatotetrafluoroethyl Heptafluoroisopropyl Ketone (I) and Fluorosulfatopentafluoroacetone (II) with Me_2S. A mixture of 4 g of keto fluorosulfate I, 2 g of Me_2S, and 10 ml of absolute diglyme was heated (90°C, 48 h) in a sealed ampul. The reaction mixture was poured into water and extracted by three 30-ml portions of ether, washed with water, and dried with $MgSO_4$, and then the ether was distilled off. Distillation of the residue over concentrated H_2SO_4 gave 2.5 g (85%) of diketone X (^{19}F NMR). It should be noted that the conversion of I was not observed at 60°C.

The analogous reaction of 5.4 g of keto fluorosulfate II and 2.8 g of Me_2S in 15 ml of diglyme followed by distillation of the reaction mixture gave 4.3 g (80%) of XI, bp 55-56°C (^{19}F NMR) [4].

Reaction of Fluorosulfatopentafluoroacetone (II) with C_6H_5ONa. A 4-g portion of keto fluorosulfate II in 15 ml of absolute monoglyme was given a gradual addition (0°C) of 1.9 g of C_6H_5ONa in 10 ml of absolute monoglyme with stirring and held at 0°C for 10 min, the reaction mass was poured into water, and the organic layer was separated, washed with water, and dried by $MgSO_4$. Distillation gave 3.5 g of a fraction with bp 78-80°C (17 mm) containing (GLC, ^{19}F NMR): 65.5% XIII, 34.5% XII. ^{19}F NMR spectrum of XIII (δ, ppm): —130.5 d. m(SO_3F), 1.9 m (CF_2), 49.7 d. m (CF, J_{CF-SO_3F} = 9.5 Hz). Mass spectrum of XII: 320 (79.2) M^+, 292 (15.6) M^+ — CO, 199 (3.8) $C_2F_4SO_3F$, 193 (3.6) M^+ — CO — SO_3F, 176 (2.3) $PhSO_3F$, 140 (1.3) PhOCOF, 97 (15.5) CF_3CO, 96 (1.4) PhF, 93 (98.4) PhO, 83 (35.2) SO_2F, 77 (49) Ph, 69 (18.4) CF_3, 65 (100) C_5H_5. ^{19}F NMR spectrum of $C^1F_3CO—C^2F_2—OSO_3Ph$ (XII) (δ, ppm): — 3.3 d(1), AB quartet centered at 0.7 with $\Delta\delta$ = 0.9, J_{1-A} = 20, J_{AB} = 258 Hz. Mass spectrum of XII: 320 (56.8) M^+, 190 (2.2) $PhCO_2CF_3$, 147 (6.5) C_2F_5CO, 143 (4.2) $PhOCF_2$, 97 (5.4) CF_3CO, 94 (6.6) PhF, 93 (100) PhO, 77 (75.1) Ph, 69 (16) CF_3, 65 (68) C_6H_5.

LITERATURE CITED

1. A. V. Fokin, A. I. Rapkin, A. S. Tatarinov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 469 (1986).
2. I. L. Knunyants, F. M. Mukhametshin, L. S. German, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1435 (1985).
3. V. M. Rogovik, N. I. Delyagina, E. I. Mysov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2057 (1990).
4. I. P. Kolenko, T. I. Filyakova, A. Ya. Zapevalov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 667 (1979).

5. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1445 (1977).
6. M. A. Kurykin, I. N. Krotovich, Yu. N. Studnev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1861 (1982).
7. M. A. Kurykin, L. S. German, Yu. N. Studnev, and A. V. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1679 (1980).
8. R. A. Bekker, G. G. Melekyan, and I. L. Knunyants, Zh. Org. Khim., 11, 1604 (1975).