(VII), bp 135° (3 mm), cf. [9]. Found: C 46.39; H 6.09; S 14.00; Si 12.16%. $C_9H_{14}O_3SSi$. Calculated: C 46.95; H 6.09; S 13.91; Si 12.17%. Infrared spectrum (ν, cm^{-1}): 770, 860, 1260 ($SiMe_3$); 1450, 2870 (CH_3); 950, 1105 (SiOS); 1190, 1350 (SO_2); 700, 750, 1485, 1590, 3075 (C_6H_5). PMR spectrum (δ, ppm): 0.44 s, 7.44-7.84 m.

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CONCLUSIONS

1. Based on the differential thermal analysis data, the chemical changes of bis(trimethylsilyl) sulfate begin at 150-170° and the formation of volatile thermolysis products at 192-200°. Among the thermolysis products were identified hexamethyldisiloxane, trimethylsilyl methylsulfonate, and tetramethyl-1,2-bis(mesyloxy)disiloxane.

2. In the presence of either metallic Na or K the thermolysis of bis(trimethylsilyl) sulfate leads only to the formation of hexamethyldisiloxane.

3. The reaction products of bis(trimethylsilyl) sulfate with trimethylphenylsilane are trimethylsilyl phenylsulfonate and hexamethyldisiloxane.

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REACTION OF FLUORINE GAS WITH IMINOESTERS OF PERFLUOROCARBOXYLIC ACIDS

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N-Fluoroiminoesters are usually obtained from other N-fluorimino acid derivatives and primarily from their acid fluorides [1]. The synthesis of these compounds by the direct fluorination of the corresponding iminoesters is not known. Only the example of obtaining the ethyl ester of N-fluorimino-p-fluorobenzoic acid by reacting trifluoromethyl hypofluorite with the iminoester of this acid is described [2].

We studied the possibility of converting the iminoesters of perfluorocarboxylic acids to the corresponding N-fluoriminoesters.

The fluorination of the methyl ester of iminotrifluoroacetic acid, diluted with fluorine, at −15 to −10°C ended in the explosive decomposition of the reaction products. Evidently the iminoester, under the influence of the HF liberated under the experimental conditions, undergoes Pinner cleavage with the formation of the corresponding amide [3].

As is known, amides when fluorinated give N,N-difluoroamides, which in the presence of

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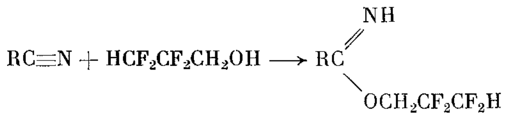
traces of moisture are hydrolyzed to the difluoroamine [4], the accumulation of which is probably responsible for the explosive decomposition of the reaction mass. In this connection we subsequently studied the reaction of fluorine with the iminoesters that were obtained from the fluorinated telomeric alcohols as described in [3]

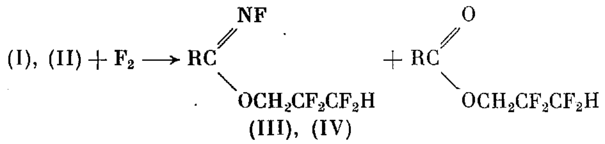


$$RC{\equiv}N + HCF_2CF_2CH_2OH \longrightarrow RC(=NH)OCH_2CF_2CF_2H$$

R = CF_3 (I), $CF(NO_2)_2$ (II).

The iminoesters from 1,1,3-trihydroperfluoropropanol were selected on the basis of the data given in [5] that they are resistant to the action of HF.

Actually, the fluorination of iminoesters (I) and (II) in a glass U-shaped reactor, packed with nickel turnings, at −5 to 0° ended in the formation of the corresponding N-fluoriminoesters (III) and (IV), together with small amounts of the esters of these acids



$$(I), (II) + F_2 \longrightarrow \underset{(III), (IV)}{RC(=NF)OCH_2CF_2CF_2H} + RC(=O)OCH_2CF_2CF_2H$$

R = CF_3 (III), $CF(NO_2)_2$ (IV).

The starting iminoesters were also detected among the fluorination products, which is apparently explained by the tying up of a part of the iminoester as the unstable hydrofluoride.

EXPERIMENTAL

The GLC analysis of the compounds was run on a 3000 × 8 mm column, packed with TND containing 5% of SE-52, while the ^{19}F NMR spectra were taken on a Perkin-Elmer R-20 instrument (56.46 MHz), using CF_3CO_2H as the standard.

The 1,1,3-trihydroperfluoropropyl esters of the iminotrifluoroacetic (I) and fluorodinitroacetic (II) acids were obtained as described in [3]. (I), bp 95-96°, n_D^{20} 1.3134; (II), bp 65° (4 mm), n_D^{20} 1.3932; colorless liquids that are heavier than water and which are soluble in ether or Freon-113, and are insoluble in water.

1,1,3-Trihydroperfluoropropyl Ester of N-Fluoriminotrifluoroacetic Acid (III). Into a reactor of the bubbler type, packed with nickel turnings, was charged 10 g (43 mmoles) of (I), which was cooled to −5° and the calculated amount of a 3:7 (by volume) F_2–N_2 mixture was passed in at −5 to 0°. At the end of fluorination the reactor was purged with N_2 and the reaction mass was fractionally distilled to give 4.8 g (45%) of (III), bp 70°, n_D^{20} 1.2915. Found: C 24.6; H 1.4; N 5.9%. $C_5H_3NF_8O$. Calculated: C 24.5; H 1.2; N 5.7%. ^{19}F NMR spectrum (δ, ppm): −94.1 s (NF), 2.6 t (CF_3), 48.6 t (CF_2), 62.6 d (CF_2H).

1,1,3-Trihydroperfluoropropyl Ester of N-Fluoriminofluorodinitroacetic Acid (IV). The same as the preceding, we obtained (IV) from (II) in 55% yield, bp 63° (4 mm), n_D^{20} 1.3809. Found: C 20.2; H 1.1; N 14.2%. $C_5H_3N_3F_6O_5$. Calculated: C 20.1; H 1.0; N 14.0%. ^{19}F NMR spectrum (δ, ppm): −53.7 s (NF), 24.3 s (CF), 47.3 t (CF_2), 61.4 d (CF_2H).

CONCLUSIONS

It was established that the corresponding N-fluoriminoesters are formed when fluorine is reacted with the 1,1,3-trihydroperfluoropropyl esters of iminoperfluorocarboxylic acids.

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