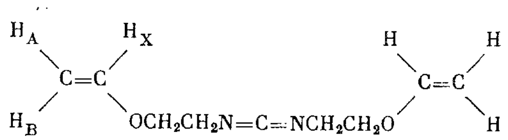

PMR spectrum (δ, ppm): 3.41 t (4H, NCH_2), 3.77 t (4H, OCH_2), 4.00 d.d (2H, H_A), 4.19 d.d (2H, H_B), 6.45 q (2H, H_X), J, Hz: 6.9 (H_AH_X), 14.3 (H_BH_X), 1.9 (H_AH_B). ^{13}C NMR spectrum (δ, ppm): 46.26 (NCH_2), 68.54 (OCH_2), 87.25 (C_β), 141.87 (N=C=N), 151.51 (C_α).

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FLUORINE-CONTAINING α-HYDROTHIONYL FLUORIDES*

R. A. Bekker† and V. Ya. Popkova

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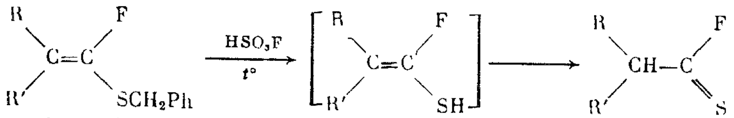
A method has been found for the synthesis of fluoride-containing α-hydrothionyl fluorides by heating polyfluoroalkenyl benzyl sulfides having fluoride atoms in the α-position relative to the sulfur atom with fluorosulfonic acid. The reactions of the acid fluorides obtained with secondary amines were studied. The reaction of the α-hydrotetrafluorothiopropionyl fluoride with $NH(Me)_2$ leads to the amide of the corresponding acid, while the product of α-hydrohexafluorothioisobutyryl fluoride with diethylamine is the dimer of bis(trifluoromethyl)thioketene.

The acid hydrolysis of perhaloalkenyl benzyl sulfides is a method for the synthesis of perhalogenated enethiols, which are the kinetically stable forms of the corresponding thioketones [3]. However, in the present work, we have shown that if perhaloalkenyl benzyl sulfides (Ia)-(Ic) with a fluorine atom in the α-position relative to the sulfur atom are subjected to hydrolysis, the final reaction products are not enethiols but rather α-thionyl fluorides (IIa)-(IIc).



(I a — c) (A) (II a — c)

R = R' = CF_3 (a), R = CF_3, R' = F (b), R = F, R' = Cl (c)

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*For previous communication, see [1]. Another communication appeared after the submission of our manuscript [1] on the synthesis of an analogous class of compounds [2].

†Deceased.

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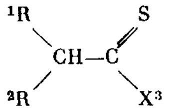
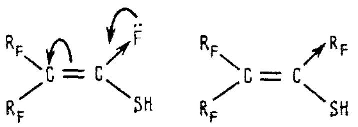
TABLE 1. ^{19}F and ^1H NMR Spectra of Compounds with the General Formula



Compound	R^1	R^2	X^3	^{19}F and ^1H										
				δ^1	δ^2	δ^3	δH	δCH_3	J_{1-2}	J_{1-3}	J_{2-3}	$J_{1\text{-}H}$	$J_{2\text{-}H}$	$J_{3\text{-}H}$
(IIb)	CF_3	F	F	4,9 d.d.d	117,1 d.d.q	−141,8 d.q	4,6 d.q.	–	13,2	7,5	55,6	6,0	45,2	–
(IIc) (in CCl_4)	Cl	F	F	–	55,6 d.d	−136,8 d.d	6,5 d.d	–	–	–	45,2	–	50,7	3,8
(III) (in CCl_4)	CF_3	F	$N(CH_3)_2$	−4,9 d.d	99,6 d.q	–	5,9 d.q	3,5 s	13,2	–	–	6,0	47,1	–

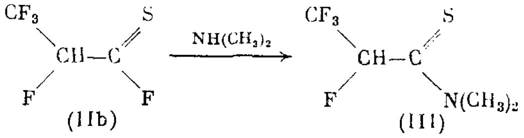
It would appear that this transformation takes place though the intermediate formation of enethiols (A), which lack kinetic stability and isomerize during the reaction to the thermodynamically more stable thiocarbonyl forms, namely, α-hydrothionyl fluorides.

The low kinetic stability of enethiols (A) in comparison with the enethiols having a perfluoroalkyl group in the α-position relative to the sulfur atom [3] may be attributed to the strong positive mesomeric effect of the vinyl atom, which enhances the electron density of the double bond and facilitates the protonation of the β-carbon atom of the CCS triad.

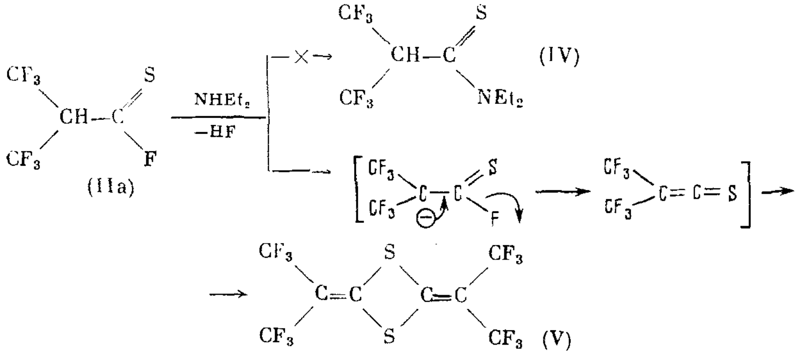


Polymers derived from fluorocarbonyl compounds have useful properties [4]. Thus, the new convenient method proposed for the preparation of fluorine-containing α-hydrothionyl fluorides in 60-80% yield augments the reported methods involving the radical addition of hydrogen sulfide to fluoorolefins by the action of x-ray or UV radiation with subsequent dehydrofluorination of the mercaptans formed by sodium fluoride [5,6] and the thermolysis of S-octafluoroisobutyl dithiophosphate and thiobenzoate in 36 and 7% yields [7].

We studied the reaction of the acid fluorides obtained with secondary amines and showed that acid fluoride (IIb), as expected, is readily converted upon reaction with dimethylamine to the dimethylamide of α-hydrotetrafluorothiopropionic acid (III).



However, the reaction of (IIa) with diethylamine leads not to the corresponding diethylamide (IV), as might have been expected, but rather to the dimer of bis(trifluoromethyl)thioketene (V), which is the major product in the reaction of (IIa) with KOH in water.

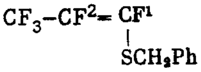


Such a discrepancy for acid fluorides (IIa) and (IIb) in their reactions with secondary amines may be attributed to the reduced CH-acidity of (IIb) (due to the Hine effect [8,9]) in comparison with acid fluoride (IIa).

The starting polyfluoroalkylenyl benzyl sulfides (Ia)-(Ic) were obtained by the reaction of the corresponding terminal F-olefins with benzyl mercaptan in the presence of Et_3N with subsequent dehydrofluorination by the action of basic reagents.

EXPERIMENTAL

The ^{19}F and ^1H NMR spectra (δ, ppm, J, Hz) were obtained on an R-32 Perkin-Elmer spectrometer at 84.6 and 90 MHz, respectively. CF_3CO_2H was the external standard for the ^{19}F NMR spectra, while TMS was the external standard for the ^1H NMR spectra. The IR spectra were taken on a UR-20 spectrometer. The purity of the products was monitored by gas-liquid chromatography on an LKhM-8MD (model 3) chromatograph using a column packed with 20% QF on Chromaton. The mass spectrum of (IIb) was taken on an MKh1303 mass spectrometer at 30 eV. The ^{19}F and ^1H NMR spectra for (IIb), (IIc), and (III) are given in Table 1.

1-Benzylthioperfluoro-1-propene (Ib). A mixture of 33.8 g (0.27 mole) $PhCH_2SH$, 70 g (0.47 mole) perfluoropropylene, and 3 ml (2.17 g, 0.02 mole) Et_3N was agitated in a steel autoclave at about 20°C for 72 h. Then, the contents of the autoclave were poured into water. The organic layer was separated and dried over $MgSO_4$. Distillation gave 32.07 g of a mixture of (Ib) and 1-benzylthio-2-hydroperfluoropropane, bp 58-68°C (3 mm). The mixture obtained was distilled over excess solid KOH in vacuum at 50 mm and dried over $MgSO_4$. Redistillation gave 21.67 g (31.3%) (Ib), bp 53-54°C (3 mm). ^{19}F NMR spectroscopy indicated that this product was a 1:2 ratio of the cis and trans isomers. Found: C, 47.54; H, 2.78; F, 37.67; S, 12.60%. Calculated for $C_{10}H_7F_5S$: C, 47.24; H, 2.78; F, 37.37; S, 12.61%. IR spectrum (ν, cm^{-1}): 1680 (C=C). ^{19}F NMR spectrum for the trans isomer: −10.0 d.d (CF_3), 42.9 d.q (F^1), 78.0 d.q (F^2);  $CF_3{-}CF^2{=}\underset{\displaystyle SCH_2Ph}{CF^1}$ $J_{CF_3-F^1} = 22.6$, $J_{CF_3-F^2} = 11.3$, $J_{F^1-F^2} = 144.8$ Hz; cis isomer: −12.4 t (CF_3), 22.4 q.d (F^1), 58.9 q.d (F^2); $J_{CF_3-F^1} = J_{CF_3-F^2} = 10.3$, $J_{F^1-F^2} = 4.7$ Hz.

α-Hydrohexafluorothioisobutyryl Fluoride (IIa). A sample of 5.2 g 1-benzylthioperfluoro-2-methyl-1-propene [10] was added dropwise to 1.5 ml freshly distilled FSO_3H. The reaction mixture was heated to 80-140°C and the product was collected in a trap cooled to −78°C. Redistillation gave 3.0 g (82.0%) (IIa), bp 42-43°C [7]. The ^{19}F NMR spectrum of this product coincided with the reported data [7].

α-Hydrotetrafluorothiopropionyl Fluoride (IIb). By analogy to the preceding procedure, 4.9 g (Ib) and 1.1 ml FSO_3H gave 1.9 g (60.0%) (IIb), bp 31-33°C. Mass spectrum (m/z, ion): 164 M^+, 144 $[M - HF]^+$, 126 $[M - 2F]^+$, 100 $[CF_3CF]^+$, 76 $[C_2HFS]^+$, 63 $[CFS]^+$.

Fluorochlorothioacetyl Fluoride (IIc). By analogy to the preceding procedure, 1.7 g 1-benzylthio-1,2-difluoro-2-chloroethylene [10] and 0.6 ml FSO_3H gave 0.7 g (68.0%) (IIc), bp 56°C [5].

Dimethylamide of α-Hydrotetrafluorothiopropionic Acid (III). A sample of 1.22 g (IIb) was added dropwise to 5 ml liquid $NH(CH_3)_2$ in a flask equipped with a dry ice condenser at −78°C. The mixture was warmed to about 20°C and ether was added. The organic layer was separated, dried over $MgSO_4$, and distilled to give 0.7 g (50.0%) (III), bp 48-49°C (4 mm). Found: C, 31.47; H, 3.69; F, 40.01%. Calculated for $C_5H_7F_4SN$: C, 31.74; H, 3.73; F, 40.17%.

Dimer of Bis(trifluoromethyl)thioketene (V). A sample of 1.0 g (IIa) was added dropwise to 6 ml abs. $NHEt_2$ cooled to −78°C. The mixture was then warmed to about 20°C and poured into water. The precipitate formed was dissolved in ether and dried over $MgSO_4$ to give 0.62 g (68.0%) (V), mp 80-82°C (from hexane) [11]. The ^{19}F NMR and IR spectra coincided with the reported data [11].

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