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1,1-Dichloropolyfluoroalkanesulfenamides and Their Dehydrochlorination Effected by Triethylamine

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Abstract—Reactions of 1,1-dichloropolyfluoroalkanesulfenyl chlorides with ammonia afford 1,1-dichloropolyfluoroalkanesulfenamides that under the action of triethylamine are converted into 3,5-bispolyfluoroalkyl-1,2,4-thiadiazoles.

Reactions of α-chloroalkanesulfenyl chlorides with ammonia and amines are studied in detail only by an example of trichloromethanesulfenyl chloride [1]. In contrast to alkane- and arenesulfenamides arising in reaction of the corresponding sulfenyl chlorides with ammonia and primary amines, the trichloromethanesulfenamides are very unstable. For instance, CCl_3SNH_2 is stable only below –70°C [1]. In reaction of CCl_3SCl with primary alkyl- and arylamines form sulfenamides CCl_3SNHR that are stable below 0°C, decompose at room temperature, and explode at heating [2]. However the longer perchloroalkyl substituent as well as introduction of fluorine into the molecule of sulfenamide result in considerable stabilization of the molecule. For instance, pentachloroetanesulfenamide $C_2Cl_5SNH_2$ [3] and fluorochloro-substituted sulfenamides CCl_2FSNH_2 and $CClF_2SNH_2$ [4] are heat-resistant compounds.

We report here on the synthesis of 1,1-dichloropolyfluoroalkanesulfenamides **I** and their transformation effected by triethylamine.

We formerly described a synthesis of 1,1-dichloro-2,2,3,3,4,4,-5,5-octafluoropentanesulfenyl chloride (**IIb**) by chlorination of ω-H-perfluoropentanal S,S-dibenzyldithioacetal [5]. Other initial compounds for preparation of 1,1-dichlorosulfenyl chlorides **I** are 1,1-dihydropolyfluoroalkyl benzyl sulfides **III**.

$$R_FCH_2SCH_2Ph \xrightarrow{Cl_2} R_FCCl_2SCl$$
IIIa, IIIb **IIa, IIb**

$$\xrightarrow{NH_3} R_FCCl_2SNH_2$$
Ia, Ib

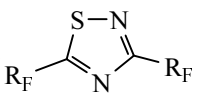
$R_F = H(CF_2)_2$ (**a**), $H(CF_2)_4$ (**b**)

The chlorination of sulfides **III** with gaseous chlorine resulted in difficultly separable mixtures of sulfenyl chlorides **II** and benzyl chloride. However passing excess ammonia through the reaction mixture afforded sulfenamides **I** that were easily separated from benzyl chloride by distillation. 1,1-Dichlorosulfenamides **I** in contrast to their nonfluorinated analogs are thermally stable liquids distillable in a vacuum.

We formerly obtained sulfenamides R_FCCl_2SNHR treating 1,1-dichloropolyfluoroalkanesulfenyl chlorides with primary aliphatic and aromatic amines. At dehydrochlorination of these compounds by lithium hexamethyldisilazide formed thermally stable C–Cl-sulfinimides $R_FC(Cl)=S=NR$ [6, 7]. The latter proved to be valuable initial compounds for preparation of fluorine-containing heterocycles [7]. This fact prompted us to investigate the dehydrochlorination of N-unsubstituted sulfenamides **I**. It was expected that at the use of an equimolar amount of a base would occur monodechlorination to afford sulfinimide $R_FC(Cl)=S=NH$.

It turned out that unlike sulfenamides R_FCCl_2SNHR whose dehydrichlorination requires the use of strong bases, 1,1-dichloropolyfluoroalkanesulfenamides **I** undergo dehydrochlorination already at treatment with triethylamine. For instance, reaction of sulfenamides **I** with triethylamine in benzene at room temperature gave rise to 3,5-bis(polyfluoroalkyl)-1,2,4-thiadiazoles **IV** in 32–40% yields.

$$R_FCCl_2-S-NH_2 \xrightarrow{Et_3N}$$
Ia, Ib



IVa, IVb

$R_F = H(CF_2)_2$ (**a**), $H(CF_2)_4$ (**b**)

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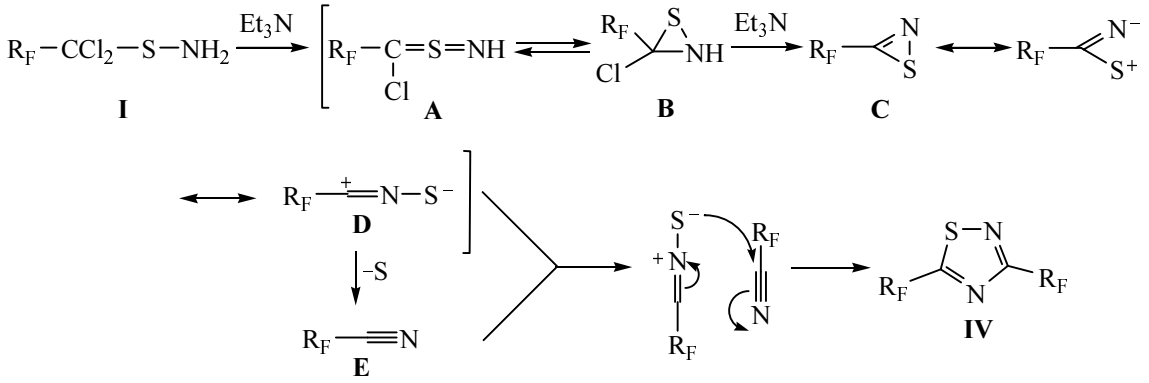
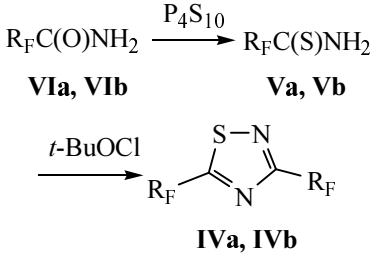
Scheme.



To elucidate the path of thiadiazoles formation the dehydrochlorination was monitored by ^{19}F NMR spectroscopy. In reaction at room temperature with 2 mol of Et_3N sulfenamide was not completely consumed even within 3 days. At the use of 3 mol of Et_3N the signals of the initial sulfenamide disappear from the ^{19}F NMR spectrum of the reaction mixture in 24 h. After disappearance of the sulfenamide signals the pattern of the ^{19}F NMR spectrum of the reaction mixture did not change even within 24 h. It is presumable that the limiting reaction stage is the primary proton abstraction from sulfenamide **I** and the arising anion quickly undergoes further transformations. Therewith it is possible that form both sulfinimide **A** and its isomer cyclic product **B** which readily undergoes further dehydrochlorination affording thiazirine **C.** The latter exists in an equilibrium with nitrile sulfide **D** [8]. Nitrile sulfides are known to be very unstable and to lose easily the sulfur to give nitriles [9]. At the same time the nitrile sulfides as active 1,3-dipoles enter into the cycloaddition reactions with nitriles. It is therefore presumable that thiadiazoles **IV** originate from nitrile sulfide addition to its decomposition product, nitrile (see the Scheme). The rate of cycloaddition is lower than that of nitrile sulfide decomposition as shows the presence in the ^{19}F NMR spectra of the reaction mixtures of signals belonging to the corresponding polyfluoroalkylnitriles, and the low-boiling nitrile $H(CF_2)_2CN$ (bp. 14°C [10]) was distilled from the reaction mixture and identified by the ^{19}F NMR spectrum.

The analogous cycloaddition of intermediately formed nitrile sulfide and nitrile was suggested as one of the possible ways of thiadiazoles formation in thioamides oxidation with *tert*-butyl hypochlorite [11]. We chose this reaction as a procedure for independent synthesis of thiadiazoles **IV** in order to confirm the structure of products obtained at sulfenamides **I** dehydrochlorination. Reactions with *tert*-butyl hypochlorite of thioamides **Va** and **Vb** that we prepared by introducing sulfur into the corresponding polyfluoroalkanecarboxamides **VIa** and **VIb** furnished thiadiazoles **IVa** and **IVb** in 54–62% yields. The physical and spectral characteristics of thus obtained compounds were identical to those of dehydrochlorination products prepared from sulfenamides **I**.



It is known that sulfinimides (of **A** type), same as nitrile sulfides (of **D** type), can react as 1,3-dipoles in the cycloaddition reactions [7, 12]. We attempted to trap the possible intermediates of the dehydrochlorination under study in the form of cycloaddition adducts. However the reactions carried out in the presence of various dipolarophiles (styrene, ethyl vinyl ether, dimethyl acetylenedicarboxylate) did not provide any new products as shown by the ^{19}F NMR spectra of the reaction mixtures. Thus the transformations of the dehydrochlorination products occur faster than the cycloaddition to the trapping agents applied.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequencies 299.943 and 282.203 MHz respectively. As internal standards served for ^1H spectra the signals of residual protons in deuterochloroform (δ_H 7.26 ppm) and for ^{19}F spectra

hexafluorobenzene (δ_F –162.9 ppm). The column chromatography was performed on silica gel Merck 60 (40–63 μm). Sulfide **IIIa** was prepared as described in [13], sulfide **IIIb** and sulfenyl chloride **IIb** by procedure from [5].

1,1-Dichloro-2,2,3,3-tetrafluoropropanesulfenyl chloride (IIa). Through a solution of 11.9 g (0.05 mol) of sulfide **IIIa** in 40 ml of chloroform at 10°C was passed a stream of gaseous chlorine for 4 h. The chloroform was distilled off on a Vigreux column first at the atmospheric pressure, then the residue was distilled in a vacuum (20 mm Hg) collecting the fraction boiling within 50–60°C. On repeated distillation the fraction was collected boiling at 50–52°C (20 mm Hg) was collected; we obtained 10 g of sulfenyl chloride **IIa**, containing 10% of benzyl chloride (according to ^{1}H NMR spectrum). Yield 72%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.59 s (Ph$\underline{CH_2}$Cl), 6.26 t.t (1H, HCF_2, $^2J_{HF}$ 52.2, $^3J_{HF}$ 5.4 Hz), 7.36 m ($\underline{Ph}CH_2Cl$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –116.1 m (2F, CF_2), –132.5 d.m (2F, CF_2H, $^2J_{FH}$ 52.2 Hz).

1,1-Dichloro-2,2,3,3,4,4,5,5-octafluoropentanesulfenyl chloride (IIb) was prepared in the same way as sulfenyl chloride **IIa** by chlorination of sulfide **IIIb**. The solvent was distilled off, the residue was distilled in a vacuum (12 mm Hg) on a Vigreux column collecting the fraction boiling at 60–65°C. Sulfenyl chloride **IIb** thus prepared contained 35% of benzyl chloride.

1,1-Dichloro-2,2,3,3-tetrafluoropropanesulfenamide (Ia). Through a solution of 16 g of a mixture of sulfenyl chloride **IIa** and benzyl chloride in 200 ml of ether gaseous ammonia was passed at –10°C for 0.5 h. The reaction mixture was stirred while gradually warmed to room temperature under continuous stream of ammonia. To the mixture 75 ml of water was added, the ether layer was separated, dried over Na_2SO_4, and the solvent was evaporated. The residue was subjected twice to a vacuum distillation. Yellow liquid. Yield 72%, bp 60–61°C (10 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.43 br.s (2H, SNH_2), 6.25 t.t (1H, CHF_2, $^2J_{HF}$ 52.8, $^3J_{HF}$ 5.7 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –117.7 m (2F, CF_2), –133.2 d.m (2F, CF_2H, $^2J_{FH}$ 52.8 Hz). Found, %: C 15.34; H 1.52; Cl 30.49; S 13.96. $C_3H_3Cl_2F_4NS$. Calculated, %: C 15.53; H 1.30; Cl 30.56; S 13.82.

1,1-Dichloro-2,2,3,3,4,4,5,5-octafluoropentanesulfenamide (Ib) [14] was prepared similarly to sulfenamide **Ia**. Yellow liquid, yield 78%, bp 89–91°C (10 mm Hg). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.58 br.s (2H, SNH_2), 5.27 t.t (1H, HCF_2, $^2J_{HF}$ 52.0, $^3J_{HF}$ 5.4 Hz). ^{19}F NMR spectrum (C_6D_6), δ, ppm: –107.6 m (2F, CF_2), –117.8 m (2F, CF_2), –129.5 m (2F, CF_2), –136.6 d.m (2F, HCF_2, $^2J_{FH}$ 52.0 Hz). Found, %: C 18.22; H 0.89; Cl 22.59; S 9.85. $C_5H_3Cl_2F_8NS$. Calculated, %: C 18.08; H 0.89; Cl 21.35; S 9.66.

Reaction of sulfenamides (I) with Et_3N. To a solution of 0.01 mol of sulfenamide **I** in 20 ml of benzene was added dropwise 4.2 ml (0.03 mol) of triethylamine, and the mixture was stirred for 24 h monitoring the completion of the reaction by disappearance in the ^{19}F NMR spectrum of the reaction mixture of the signals of the initial sulfenamide. The precipitate was filtered off, the filtrate was washed with a saturated water solution of NH_4Cl, dried over Na_2SO_4, and benzene was evaporated. The residue was subjected to fractional distillation in a vacuum. Thiadiazoles **IV** were additionally purified by column chromatography on silica gel, eluent petroleum ether, monitoring by TLC Silufol UV-254 plates, development in a iodine chamber.

3,5-Bis(2,2,3,3-tetrafluoroethyl)-1,2,4-thiadiazole (IVa). Colorless liquid, yield 40%, bp 51–53°C (10 mm Hg), R_f 0.72. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.31 t.t (1H, HCF_2, $^2J_{HF}$ 52.8, $^3J_{HF}$ 4.0 Hz), 6.35 t.t (1H, HCF_2, $^2J_{HF}$ 52.8, $^3J_{HF}$ 4.4 Hz). ^{19} F NMR spectrum ($CDCl_3$), δ, ppm: –111.3 m (2F, CF_2), –116.3 (2F, CF_2), –136.5 d.m (2F, CF_2, $^2J_{FH}$ 52.8 Hz), –137.5 d.m (2F, CF_2H, $^2J_{FH}$ 52.8 Hz). Found, %: C 25.36; H 0.68; N 9.62; S 11.00. $C_6H_2F_8N_2S$. Calculated, %: C 25.18; H 0.70; N 9.79; S 11.21.

3,5-Bis(2,2,3,3,4,4,5,5-octafluorobutyl)-1,2,4-thiadiazole (IVb). Colorless liquid, yield 32%, bp 45–47°C (0.06 mm Hg), R_f 0.64. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.10 t.t (1H, HCF_2, $^2J_{HF}$ 51.9, $^3J_{HF}$ 5.1 Hz), 6.11 t.t (1H, HCF_2, $^2J_{HF}$ 52.1, $^3J_{HF}$ 5.3 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –107.5 m (2F, $C\underline{F_2}$–C^3), –112.3 m (2F, $C\underline{F_2}$–C^5), –124.3 m (2F, CF_2), –125.2 m (2F, CF_2), –129.6 m (2F, CF_2), –130.6 m (2F, CF_2), –138.2 m (4F, 2×CF_2H). Found, %: C 24.87; H 0.59; F 61.79; N 5.68; S 6.43. $C_{10}H_2F_{16}N_2S$. Calculated, %: C 24.70; H 0.41; F 62.52; N 5.76; S 6.60.

Synthesis of thioamides V. General procedure. To a dispersion of 0.05 mol of amide **VI** in 100 ml of toluene was added 26.68 g (0.06 mol) of P_4S_{10} and 6.7 g (0.05 mol) of hexamethyldisiloxane. The mixture was heated to 80°C under vigorous stirring for 20 h with compound **VIa** or for 12 h with compound **VIb**. The precipitate was filtered off and washed on the filter with 20 ml of ether. The solvents were removed in a vacuum (10–20 mm Hg), the residue was diluted with ether (100 ml). The ether solution was washed in succession with a satu-

rated solution of $NaHCO_3$ till the end of gas evolution (4×50 ml), with a saturated solution of NaCl (2×100 ml), and with water (2×100 ml). The water layer was additionally extracted with ether (2×100 ml). The combined ether solution was dried with Na_2SO_4, the ether was removed in a vacuum (10–20 mm Hg), and the thioamides **V** were obtained as a residue.

2,2,3,3-Tetrafluorothiopropionamide (Va). Yellow liquid, yield 40%, bp 45–50°C (0.07 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.42 t.t (1H, HCF_2, $^2J_{HF}$ 53.4, $^3J_{HF}$ 5.5 Hz), 7.78 br.s (1H, NH), 8.00 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –120.5 m (2F, CF_2), –139.7 d.m (2F, CF_2H, $^2J_{FH}$ 53.4 Hz). Found, %: C 22.29; H 1.75; N 8.52; S 20.10. $C_3H_3F_4NS$. Calculated, %: C 22.36; H 1.88; N 8.69; S 19.90.

2,2,3,3,4,4,5,5-Octafluorothiovaleramide (Vb). Colorless crystals, yield 89%, mp 38–41°C (from hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 t.t (1H, HCF_2, $^2J_{HF}$ 52.0, $^3J_{HF}$ 5.3 Hz), 7.44 br.s (1H, NH), 7.91 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.8 m (2F, CF_2), –123.8 m (2F, CF_2), –130.3 m (2F, CF_2), –138.3 d.m (2F, CF_2H, $^2J_{FH}$ 52.0 Hz). Found, %: C 22.49; H 1.05; N 5.48; S 12.33. $C_5H_3F_8NS$. Calculated, %: C 23.00; H 1.16; N 5.36; S 12.28.

Synthesis of thiadiazoles IV from thioamides V. *General procedure.* To a solution of 5.4 mmol of thioamide **V** in 10 ml of chloroform was added 0.32 ml (2.7 mmol) of *tert*-butyl hypochlorite, and the reaction mixture was stirred at room temperature for 24 h. The precipitate of elemental sulfur was filtered off, the chloroform was distilled off, and the residue was distilled in a vacuum. Yield of thiadiazole **IVa** 54%, of thiadiazole **IVb** 62%.

REFERENCES

1. Koval', I.V., *Usp. Khim.,* 1991, vol. 60, p. 1645.
2. Haas, A. and Lorenz, R., *Chem. Ber*., 1972, vol. 105, p. 3161.
3. Boureghda, A., Abdel-Megeed, M.F., Ghattas, A.B.A.G., Jensen, B., and Senning, A., *Sulfur Lett*., 1987, vol. 5, p. 159.
4. Haas, A. and Lorenz, R., *Chem. Ber*., 1972, vol. 105, p. 273.
5. Markovskii, L.N., Slyusarenko, E.I., Timoshenko, V.M., Kaminskaya, E.I., Kirilenko, A.G., and Shermolovich, Yu.G., *Zh. Org. Khim.*, 1992, vol. 28, p. 14.
6. Shermolovich, Yu.G., Timoshenko, V.M., Rozhenko, A.B., and Markovskii, L.N., *Zh. Org. Khim.*, 1992, vol. 28, p. 427.
7. Ahlemann, J.-T., Roesky, H.W., Markovsky, L.N., Timoshenko, V.M., and Shermolovich, Yu.G., *Heteroatom Chem*., 1995, vol. 6, p. 9.
8. Gotthardt, H., *Tetrahedron Lett.,* 1971, vol. 12, p. 1277.
9. Paton, R.M., *Chem. Soc. Rev*., 1989, vol. 18, p. 33.
10. England, D.C., Lindsey, R.V., and Melby, L.R., *J. Am. Chem. Soc*., 1958, vol. 80, p. 6442.
11. El-Wassimy, M.T.M, Jorgensen, K.A., Lawesson, S.O., *Tetrahedron*, 1983, vol. 39, p. 1729.
12. Markovskii, L.N., Timoshenko, V.M., and Shermolovich, Yu.G., *Zh. Org. Khim.*, 1995, vol. 31, p. 161.
13. Timoshenko, V.M., Listvan, V.V., Rusanov, E.B., Shermolovich, Yu.G., and Markovskii, L.N., *Zh. Org. Khim.*, 1997, vol. 33, p. 70.
14. Timoshenko, V.M., *Cand. Sci. (Chem.) Dissertation*, Kiev, 1994.