

SHORT  
COMMUNICATIONS

## Synthesis of 1-Chloropolyfluoroalkyl Isothiocyanates

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In the synthesis of N,S-containing heterocyclic compounds are widely used 2- and 3-halogen-substituted alkyl isothiocyanates [1]. As a rule they easily undergo cyclization when treated with unfunctional nucleophilic reagents to afford derivatives of 1,3-thiazole and 1,3-thiazine [1, 2]. In their turn 1-haloalkyl isothiocyanates can cyclize only under treatment of bifunctional nucleophiles [3–5]. Up till now the latter processes are less known mostly due to the limited number of available 1-haloalkyl isothiocyanates. Yet the analysis of the chemical properties of the heteroanalogs of 1-chloroalkyl isothiocyanates, 1-chloroalkyl isocyanates [6] and 1-chloroalkylcarbodiimides [7] shows that the most valuable electrophilic synthons for cyclocondensation are heterocumulenes containing electronegative groups at the  $\alpha$ -carbon. Only few of such 1-chloroalkyl isothiocyanates are described in the literature [8, 9].

We report here on a convenient preparative synthesis of new alkyl isothiocyanates **Ia, b** containing apart  $\alpha$ -chlorine also polyfluoroalkyl substituents. The essence of the synthesis is the reaction of polyfluoro-1,1,3-trichloro-2-azaalk-1-enes (**IIa, b**) with phosphorus pentasulfide [8] that is carried out by heating the reagents in boiling toluene for 8 h. As a result the target products **Ia, b** are obtained in 50–56% yield. The initial polyfluoro-chloro-2-azaalk-1-enes **IIa, b** were prepared in 64–68% yield by treat-

ing with phosphorus pentachloride of  $\alpha$ -hydroxypolyfluoroalkylformamides **IIIa, b**. The latter compounds were obtained by condensation of polyfluoroalkylaldehydes **IVa, b** with formamide.

The assumed structure of compounds **IIa, b–IVa, b** is consistent with their IR and  $^1\text{H}$  NMR spectra.

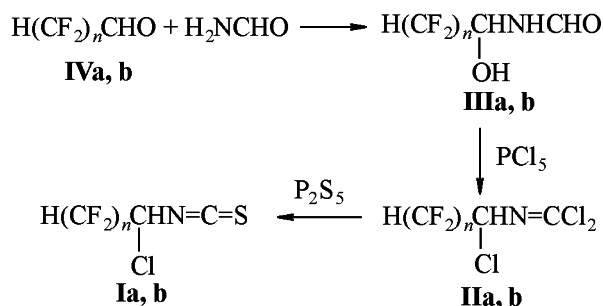
**N-(1-Hydroxypolyfluoroalkyl)formamides (IIIa, b).** Equimolar amounts (0.02 mol) of aldehyde **IVa, b** and formamide were vigorously stirred for 10–15 min. The formed homogeneous mixture was left standing for 24 h and then purified by reprecipitation with hexane from benzene (aldehyde **IVa**) or by crystallization from a mixture hexane–benzene, 1:4 (aldehyde **IVb**).

**N-(1-hydroxy-2,2,3,3,4,4,5,5-octafluoropentyl)formamide (IIIa).** Yield 93%, viscous oily fluid. IR spectrum,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ : 1680 (C=O), 3380 (OH, NH).  $^1\text{H}$  NMR spectrum  $\delta$ , ppm: 5.48 m (1H, OH), 6.12 m (1H, CHN), 6.72 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  50.0,  $^3J_{\text{HF}}$  5.1 Hz), 8.29 s (1H, CH), 8.36 m (1H, NH). Found, %: F 55.57; N 4.82.  $\text{C}_6\text{H}_5\text{F}_8\text{NO}_2$ . Calculated, %: F 55.25; N 5.09.

**N-(1-Hydroxy-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)formamide (IIIb).** Yield 94%, mp 49–51°C (hexane–benzene, 1:4). IR spectrum, KBr,  $\text{cm}^{-1}$ : 1675 (C=O), 3370 (OH, NH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 5.40 m (1H, OH), 6.18 m (1H, CHN), 6.88 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  51.0,  $^3J_{\text{HF}}$  5.1 Hz), 8.40 s (1H, CH), 8.43 m (1H, NH). Found, %: F 61.12; N 4.04.  $\text{C}_8\text{H}_5\text{F}_{12}\text{NO}_2$ . Calculated, %: F 60.78; N 3.73.

**Polyfluoro-1,1,3-trichloro-2-azaalk-1-enes (IIa, b).** A mixture of 0.01 mol of *N*-(1-hydroxypolyfluoroalkyl)formamide **IIIa, b** and 0.03 mol of phosphorus pentachloride was heated to 120°C for 5 h, the mixture was cooled in a flow of dry sulfur dioxide and fractionated.

**2-Aza-2,2,3,3,4,4,5,5-octafluoro-1,1,3-trichlorohept-1-ene (IIa).** Yield 66%, bp 68–71°C (12 mm Hg)



I–IV,  $n = 4$  (a), 6 (b).

$n_D^{20}$  1.3682. IR spectrum,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ : 1645 ( $\text{C}=\text{N}$ ).  $^1\text{H}$  NMR spectrum  $\delta$ , ppm: 5.74 d.d (1H,  $\text{CHCl}$ ,  $^3J_{\text{HFA}}$  12.3,  $^3J_{\text{HFB}}$  13.5 Hz), 6.20 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  48.0,  $^3J_{\text{HF}}$  5.3 Hz). Found, %: Cl+F 74.57.  $\text{C}_6\text{H}_2\text{Cl}_3\text{F}_8\text{N}$ . Calculated, %: Cl+F 74.89.

**2-Aza-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1,1,3-trichloronon-1-ene (IIb).** Yield 63%, bp 90–94°C (12 mm Hg),  $n_D^{20}$  1.3705. IR spectrum,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ : 1645 ( $\text{C}=\text{N}$ ).  $^1\text{H}$  NMR spectrum  $\delta$ , ppm: 5.69 d.d (1H,  $\text{CHCl}$ ,  $^3J_{\text{HFA}}$  12.6,  $^3J_{\text{HFB}}$  13.6 Hz), 6.14 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  49.0,  $^3J_{\text{HF}}$  5.3 Hz). Found, %: Cl+F 74.43.  $\text{C}_8\text{H}_2\text{Cl}_3\text{F}_{12}\text{N}$ . Calculated, %: Cl+F 74.89.

**1-Chloropolyfluoroalkyl isothiocyanates Ia, b.** A mixture of 0.006 mol of polyhalo-2-azaalk-1-ene **IIa, b** and 0.002 mol of phosphorus pentasulfide in 50 ml of toluene was heated at boiling and stirring for 8 h. The precipitate was filtered off, and the filtrate was subjected to fractional distillation in a vacuum.

**2,2,3,3,4,4,5,5-Octafluoro-1-chloropentyl isothiocyanate (Ia).** Yield 56%, bp 69–71°C (12 mm Hg),  $n_D^{20}$  1.4929 (Ia). IR spectrum,  $\text{CCl}_4$ ,  $\text{cm}^{-1}$ : 2050 ( $\text{N}=\text{C}=\text{S}$ ).  $^1\text{H}$  NMR spectrum  $\delta$ , ppm: 5.71 d.d (1H,  $\text{CHCl}$ ,  $^3J_{\text{HFA}}$  12.0,  $^3J_{\text{HFB}}$  5.6 Hz), 5.96 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  51.6,  $^3J_{\text{HF}}$  5.6 Hz). Found, %: Cl + F 61.27; S 10.28.  $\text{C}_6\text{H}_2\text{ClF}_8\text{NS}$ . Calculated, %: Cl + F 60.94; S 10.42.

**2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoro-1-chloroheptyl isothiocyanate (Ib).** Yield 50%, bp 92–95°C (12 mm Hg),  $n_D^{20}$  1.4820. IR spectrum,  $\text{CCl}_4$ ,  $\text{cm}^{-1}$ : 2055 ( $\text{N}=\text{C}=\text{S}$ ).  $^1\text{H}$  NMR spectrum  $\delta$ , ppm: 5.72 d.d (1H,  $\text{CHCl}$ ,  $^3J_{\text{HFA}}$  12.0,  $^3J_{\text{HFB}}$  5.6 Hz), 5.97 t.t (1H,  $\text{CHF}_2$ ,  $^2J_{\text{HF}}$  51.8,  $^3J_{\text{HF}}$  5.6 Hz). Found, %: Cl + F 64.40; S 8.11.  $\text{C}_8\text{H}_2\text{ClF}_{12}\text{NS}$ . Calculated, %: Cl + F 64.63; S 7.87.

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