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Polyfluorinated hydrazones in organic syntheses
3.* Reactions of poly- and perfluoroaldehyde hydrazones with hydrazine hydrate

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The reaction of poly- and perfluoroaldehyde hydrazones with hydrazine hydrate was studied. A new preparative method for obtaining the hitherto inaccessible *N,N*-unsubstituted bis-hydrazones of polyfluorinated α-oxoaldehydes was developed based on this reaction.

Key words: hydrazine hydrate, 7-H-dodecafluoroheptanal, poly- and perfluoroaldehyde hydrazones, polyfluorinated α-oxoaldehyde bis-hydrazones.

The interaction of *N,N*-unsubstituted hydrazones of monocarbonyl compounds with hydrazine hydrate usually results in their reduction to hydrocarbons.[1] We have studied for the first time the behavior of fluorine-containing analogs in this reaction, with perfluoropentanal hydrazone as an example, and have obtained, in a low yield, *N,N*-unsubstituted perfluoropropylglyoxal bis-hydrazone, the first fluorine-containing representative of such compounds.[2]

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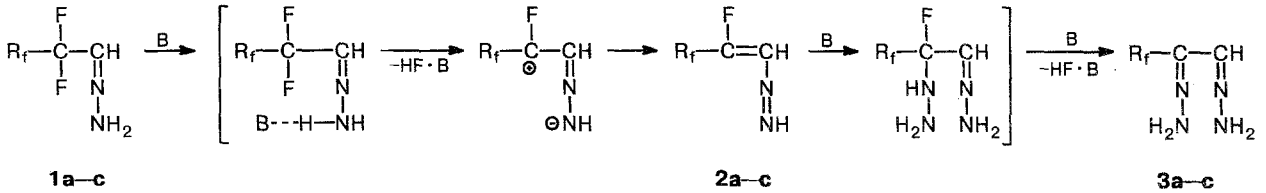
The present work deals with the reaction of poly- and perfluoroaldehyde hydrazones with hydrazine hydrate with the purpose of synthesizing new compounds belonging to this class.

The reactions of perfluoro- (**1b**) and 7-H-dodecafluoroheptanal hydrazone (**1c**) with hydrazine hydrate gave hitherto unknown perfluoro- (**3b**) and 5-H-decafluoropentylglyoxal bis-hydrazones (**3c**) in high yields (Scheme 1). The reaction occurred in methanol; no less than 3 mol.-equiv. hydrazine hydrate was used, of which 2 mol.-equiv. were consumed to bind HF. The transformation of hydrazone (**1a**) into bis-hydrazone

Scheme 1



1a–c **2a–c** **3a–c**

$R_f = C_3F_7$ (**a**), C_5F_{11} (**b**), $CHF_2(CF_2)_4$ (**c**); B = $N_2H_4 \cdot H_2O$

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(**3a**) also occurred in a higher yield than reported previously.[2]

The formation of bis-hydrazones **3a—c** probably occurs due to dehydrofluorination of monohydrazones **1a—c** in the presence of hydrazine hydrate as a base. The resulting azoolefins (**2a—c**) react with the second equivalent of hydrazine hydrate and give **3a—c** following dehydrofluorination.

The bis-hydrazones obtained are stable and can be stored under ordinary conditions. They can be chromatographed at temperatures below 200 °C. Their structures were confirmed by ^1H, ^{19}F NMR, and IR spectroscopy and mass spectrometry.

The above results suggest that, irrespective of the chain length of the substituent in the starting hydrazone, the reaction occurs stereoselectively, has general applicability, and can serve as a convenient method for obtaining compounds of this class.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Perkin-Elmer 32 spectrometer (90 and 84.6 MHz, respectively) using $SiMe_4$ and CF_3COOH as external standards. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra (EI, 70 eV) were obtained on a 7070 E chromato-mass spectrometer.

The starting hydrazones **1a** and **1b** were synthesized by a known procedure,[2] and hydrazone **1c** was obtained from 7-H-dodecafluoroheptanal hydrate and hydrazine hydrate in ~70 % yield.

7-H-Dodecafluoroheptanal hydrazone (1c). A solution of 7-H-dodecafluoroheptanal hydrate (6 g, 17 mmol) in EtOH (5 mL) was added to a solution of hydrazine hydrate (1.3 g, 26 mmol) in EtOH (5 mL), and then glacial CH_3COOH (1.5 g, 26 mmol) was added. The mixture was kept for one day at room temperature (the reaction was monitored by ^{19}F NMR spectroscopy) and diluted with water. The organic layer was separated and distilled *in vacuo* to give 4.2 g (70 %) of monohydrazone **1c**, b.p. 80—82 °C (1 Torr). The residue contained 1 g of a solid compound, which was not studied further. IR, ν/cm^{-1}: 1620 s (C=N); 3040 w (CH); 3240, 3340 and 3450 s (NH_2). ^1H NMR (CCl_4), δ: 7.1 (t, 1 H, $CF_2CH{=}N$, J = 7.5 Hz); 6.7 (s, 2 H, NH_2); 6.15 (tt, 1 H, HCF_2CF_2, J = 52.5 Hz). ^{19}F NMR, δ: 38.02 (m, 2 F, CF_2); 46.10 (m, 2 F, CF_2); 48.20 (m, 4 F, 2 CF_2); 55.20 (tm, 2 F, CF_2); 62.00 (dm, 2 F, CF_2H, J = 52.5 Hz). Found (%): C, 24.61; H, 1.30; N, 8.46; F, 65.94. $C_7H_4F_{12}N_2$. Calculated (%): C, 24.41; H, 1.16; N, 8.13; F, 66.28. MS, *m/z* (*I* (%)): 344 $[M]^+$ (31), 325 $[M-F]^+$ (25), 298 $[H(CF_2)_6]^+$ (3), 248 $[H(CF_2)_5]^+$ (2), 174 $[C_4H_3F_5N_2]^+$ (3), 124 $[C_3H_3F_3N_2]^+$ (3), 69 $[CF_3]^+$ (19), 51 $[CF_2H]^+$ (19), 43 $[CH{=}NNH_2]^+$ (100).

Perfluoropropylglyoxal bis-hydrazone (3a). A solution of hydrazine hydrate (11 g, 220 mmol) in MeOH (25 mL) was added to a solution of hydrazone **1a** (15.6 g, 60 mmol) in MeOH (50 mL). The mixture was kept at room temperature until the reaction ceased (20 h). The end of the reaction was determined from disappearance of the starting compound **1a** in the reaction mixture (^{19}F NMR data). The mixture was diluted with water, and the organic layer was separated and quickly distilled *in vacuo* with heating in the flame of a gas burner to give 11.9 g (78 %) of bis-hydrazone **3a**, b.p. 104—105 °C (10 Torr), which was identical with an authentic sample (according to ^{19}F NMR data and the b.p.).[2]

Perfluoropentylglyoxal bis-hydrazone (3b). Similarly, starting from compound **1b** (43.4 g, 120 mmol) and hydrazine hydrate (24 g, 480 mmol), bis-hydrazone **3b** (33 g, 79 %) was obtained, b.p. 106—108 °C (1 Torr). IR, ν/cm^{-1}: 1580, 1600 and 1640 s (C=N); 2960 w (CH); 3240 m and 3450 vs (NH_2). ^1H NMR (CD_3Cl), δ: 5.75 (s, 2 H, H_2N); 7.48 (s, 1 H, HC=N); 8.88 (br.s, 2 H, H_2N). ^{19}F NMR (CD_3Cl), δ: 3.2 (tm, 3 F, CF_3); 34.0 (tm, 2 F, CF_2); 44.7 (m, 4 F, 2 CF_2); 48.7 (m, 2 F, CF_2). Found (%): C, 24.04; H, 1.33; N, 16.31; F, 59.22. $C_7H_5F_{11}N_4$. Calculated (%): C, 24.01; H, 1.41; N, 15.81; F, 59.04. MS, *m/z* (*I* (%)): 354 $[M]^+$ (45.10), 338 $[M-NH_2]^+$ (12.62), 337 $[M-NH_3]^+$ (9.38), 335 $[M-F]^+$ (5.64), 326 $[M-N_2]^+$ (11.87), 311 $[M-CH{=}NNH_2]^+$ (6.91), 309 $[M-N_3H_3]^+$ (5.33), 119 $[C_2F_5]^+$ (16.58), 92 $[CF_2C{=}NNH_2]^+$ (7.92), 87 $[CF{=}CHCH{=}NNH_2]^+$ (20.13), 85 $[H_2NN{=}CHC{=}NNH_2]^+$ (5.22), 69 $[CF_3]^+$ (46.04), 68 $[C_2H_2N_3]^+$ (12.29), 43 $[CH{=}NNH_2]^+$ (100.00), 42 $[C{=}NNH_2]^+$ (12.43), 32 $[N_2H_4]^+$ (30.99), 31 $[N_2H_3]^+$ (35.42), 30 $[N_2H_2]^+$ (18.41), 29 $[N_2H]^+$ (13.31), 28 $[N_2]^+$ (14.36), 17 $[NH_3]^+$ (9.07).

5-H-Decafluoropentylglyoxal bis-hydrazone (3c). A similar procedure starting from compound **1c** (3.1 g, 9 mmol) and hydrazine hydrate (2 g, 40 mmol) in MeOH (40 mL) gave 2.5 g (80 %) of bis-hydrazone **3c**, b.p. 137 °C (3 Torr). IR, ν/cm^{-1}: 1580, 1600, and 1640 s (C=N); 2940 and 3030 w (CH); 3240 and 3430 vs (NH_2). ^1H NMR, δ: 9.30 (br.s, 2 H, H_2N); 7.65 (s, 1 H, CH=N); 6.15 (tm, 1 H, $HCF_2(CF_2)_4$, J = 53 Hz); 5.95 (s, 2 H, NH_2). ^{19}F NMR, δ: 39.0 (tm, 2 F, CF_2); 46.35 (tm, 2 F, CF_2); 47.40 (m, 2 F, CF_2); 57.25 (m, 2 F, CF_2); 62.15 (dm, 2 F, CF_2H, J = 52 Hz). MS, *m/z*: 336 $[M]^+$, 320 $[M-NH_3]^+$, 308 $[M-N_2]^+$, 293 $[H(CF_2)_5C{=}NNH_2]^+$, 278 $[H(CF_2)_5C{=}NH]^+$, 137 $[CF_2CF{=}CHCH{=}NNH_2]^+$, 118 $[C_3H_2N_3F_2]^+$, 90 $[CF_2CN_2]^+$, 87 $[CF{=}CHCH{=}NNH_2]^+$, 69 $[CF_3]^+$, 51 $[HCF_2]^+$, 43 $[CH{=}NNH_2]$. Found (%): C, 25.24; H, 1.44; N, 16.23. $C_7H_6F_{10}N_4$. Calculated (%): C, 25.10; H, 1.73; N, 16.55.

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