ELSEVIER

Journal of Fluorine Chemistry 79 (1996) 39–43

JOURNAL OF FLUORINE CHEMISTRY

Bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds

G.G. Bargamov *, M.D. Bargamova

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russia

Received 3 November 1995; accepted 24 March 1996

Abstract

New preparative methods are described for obtaining *N,N*-unsubstituted bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds from hydrazine hydrate and easily available polyfluoroaldehydes or perfluoro-4-methyl-2-pentene.

Keywords: Hydrazine hydrate; Hydrates of polyfluoroaldehydes; Hydrazones of poly- and per-fluoroaldehydes; Bis-hydrazones of polyfluoroalkyl α-ketoaldehydes; Perfluoro-4-methyl-2-pentene; 1,1,1,5,5,5-Hexafluoro-4-trifluoromethyl-2,3-pentanedione bis-hydrazone

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1. Introduction

Bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds may be of interest as synthones for the introduction of perfluoroalkyl groups into various desired structures. However, such compounds had not been reported until our studies.

Non-fluorinated analogues of bis-hydrazones are well known and usually condensation of α-dicarbonyl compounds with hydrazine hydrate is used for their preparation [1]. Attempts to extend this reaction to polyfluorinated α-dicarbonyl compounds failed: only products of their haloform decomposition were isolated in this reaction [2]. Attempts to isolate a bis-hydrazone from the reaction of hydrazine hydrate with perfluoro-2-butene also failed [3].

The present study was devoted to the reactions of poly- and per-fluoroaldehyde hydrates and perfluoro-4-methyl-2-pentene with hydrazine hydrate in order to synthesize bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds.

2. Results and discussion

Earlier, one of us showed that a monocarbonyl compound containing a difluoromethylene group at the α-position behaved like an α-dicarbonyl compound in the reaction with an excess of phenylhydrazine at elevated temperature and was converted to bis-phenylhydrazone [4] (see Scheme 1).

The CF_2 group next to the activating aldehyde group behaves like a carbonyl group in this reaction, i.e. it is a formal analogue of the C=O group.

Using this fact we succeeded in demonstrating that a similar conversion occurred in the case of hydrazine hydrate (which is a weaker base than phenylhydrazine) to yield bis-hydrazones. Thus, when perfluoropentanal (**1a**) reacts with an excess of hydrazine hydrate under the conditions reported in Ref. [4] at elevated temperature, the bis-hydrazone of perfluoropropylglyoxal (**4a**) is formed in ca. 30% yield.

The formation of the bis-hydrazone **4** is explained by dehydrofluorination of the monohydrazone **2** in the presence of a base, hydrazine hydrate; the azolefin **3** formed in this case reacts with a second mole of hydrazine hydrate, and the ensuing dehydrofluorination gives product **4**.

The low yield of the bis-hydrazone **4a** in this process is attributed to its conversion to another product (**5**) under the reaction conditions. Bis-hydrazone **4a** is readily converted to compound **5** when heated at ca. 140 °C or distilled slowly in vacuo [5].

$$2\,(\mathbf{4a}) \xrightarrow[-N_2H_4]{} \mathbf{5}$$

We are at present refining the structure of compound **5**, to which one of the possible structures **5a** (as reported in Ref. [5]), **5b** or **5c** may be assigned based on the IR, NMR (^1H and ^{19}F) and mass spectra.

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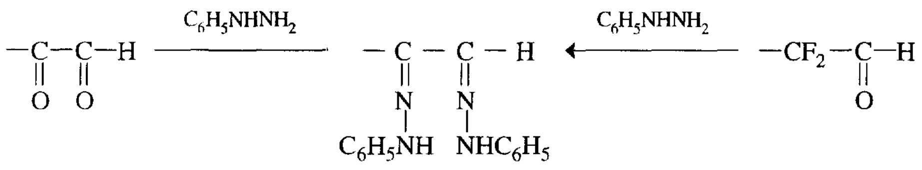
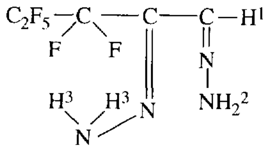
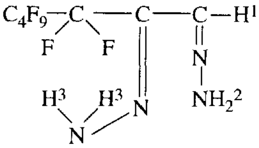
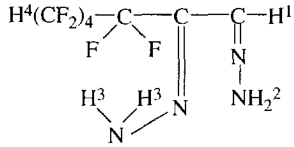
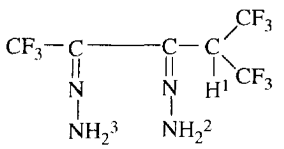
* Corresponding author.

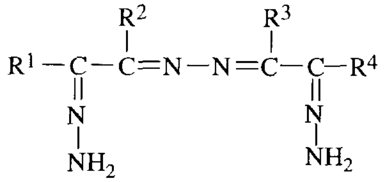
PII S0022-1139(96)03445-8



Scheme 1.

Table 1
^{1}H NMR spectra of compounds **4a**, **4b**, **4c** and **10**

Compound	Solvent	δH^1 (ppm); J (Hz)	δH^2 (ppm)	δH^3 (ppm)	δH^4 (ppm); J (Hz)
 (**4a**)	no solvent	7.33	5.77	8.95	
 (**4b**)	$CDCl_3$	7.48	5.75	8.88	
 (**4c**)	no solvent	7.65	5.95	9.30	6.15 tt; $J=53$
 (**10**)	CCl_4	3.82 hept; $J=10$	6.12	6.30	



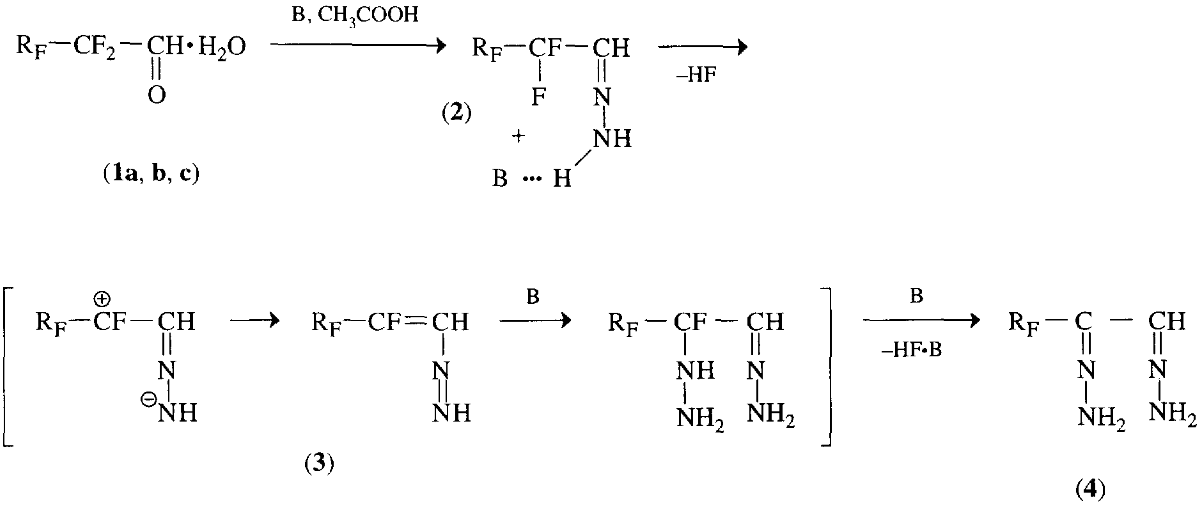
$R^1-C(=N-NH_2)-C(R^2)=N-N=C(R^3)-C(=N-NH_2)-R^4$

(**5**)

[**5a** ($R^1 = R^4 = C_3F_7$; $R^2 = R^3 = H$);
5b ($R^1 = R^3 = C_3F_7$; $R^2 = R^4 = H$);
5c ($R^1 = R^4 = H$; $R^2 = R^3 = C_3F_7$)]

We have found that the yield of the bis-hydrazone **4a** increases significantly and becomes almost quantitative when conversions of perfluoropentanal hydrate are carried out in two successive steps: (1) conversion to the monohydrazone **2a** and (2) subsequent conversion to the bis-hydrazone **4a** under mild conditions with monitoring of the hydrazine hydrate used [5]. Hydrazones of perfluoroheptanal (**2b**) and 7-*H*-heptanal (**2c**) have been obtained from hydrates of perfluoroheptanal (**1b**) and 7-*H*-heptanal (**1c**) in a similar manner. Hydrazones **2b** and **2c** are converted to the bis-hydrazones of perfluoropentylglyoxal (**4b**) and 7-*H*-decafluoro-pentylglyoxal (**4c**) when they react with hydrazine hydrate. The reaction is carried out at room temperature in methanol and requires at least a three-fold molar excess of hydrazine hydrate, two of the three moles being used to bind the HF liberated in this reaction.

The data obtained show that the reaction occurs regioselectively independent of the substituent chain length in the starting aldehyde. The reaction is of a general character and

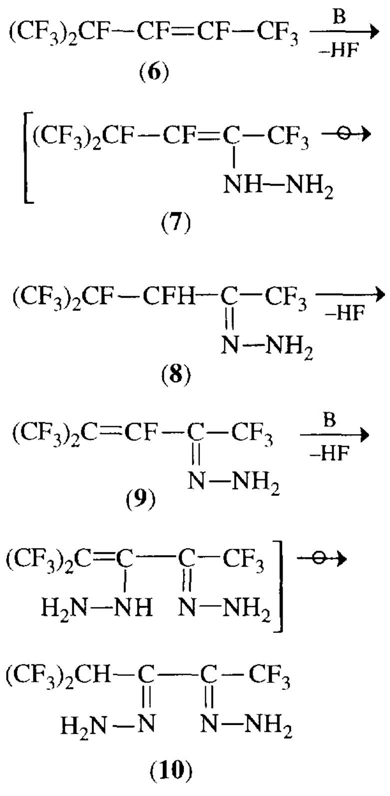


[$R_F = C_3F_7$(**a**); C_5F_{11} (**b**); $HCF_2(CF_2)_4$ (**c**). $B = N_2H_4{\cdot}H_2O$]

can be used as a convenient method for the synthesis of substances of this class.

To obtain bis-hydrazones of aliphatic polyfluorinated α-diketones, we studied the reaction of perfluoro-4-methylpentene-2 (**6**) with hydrazine hydrate (see Preliminary Communication [6]).

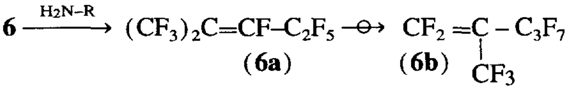
It turned out that the interaction of olefin **6** with hydrazine hydrate in ethanol or monoglyme gave the bis-hydrazone of 1,1,1,5,5,5-hexafluoro-4-trifluoromethyl-2,3-pentane-dione (**10**).



($B = N_2H_4{\cdot}H_2O$)

The process involves a number of successive steps: nucleophilic substitution of the vinyl fluorine atom, isomerization of the intermediate enehydrazine **7**, dehydrofluorination of the monohydrazone **8** and a similar conversion of olefin **9** with the second equivalent of hydrazine hydrate.[1]

It was shown previously that when olefin **6** reacted with nucleophilic reagents, for example, with amines [7], it pre-isomerized into perfluoro-2-methyl-2-pentene (**6a**) or perfluoro-2-methyl-1-pentene (**6b**); this results in the products of the interaction of amines with olefins **6a** or **6b**, and sometimes their mixture.



$$6 \xrightarrow{H_2N-R} \underset{(\mathbf{6a})}{(CF_3)_2C{=}CF{-}C_2F_5} \rightleftharpoons \underset{(\mathbf{6b})}{CF_2{=}\underset{CF_3}{C}{-}C_3F_7}$$

In our case, the formation of bis-hydrazone **10** was possible because of the lack of such isomerization. It should be noted that compound **10** is the first representative of α-bis-hydrazones of aliphatic polyfluorinated α-diketones.

The bis-hydrazones obtained are stable under conventional conditions and can be studied by GLC methods. The structure of these compounds was assigned on the basis of their IR, NMR (^1H and ^{19}F) and mass spectra. The ^1H NMR spectra of compounds **4a, 4b** and **4c**, and **10** contain three principal groups of signals (see Table 1). The singlets at 7.33, 7.48, 7.65 ppm and 5.77, 5.75, 5.95 ppm correspond respectively to the H^1 and H^2 protons of the $H^1\underset{|}{C}{=}N{-}NH_2{}^2{-}$ group in the bis-hydrazones **4a, 4b** and **4c**. A broadened signal at 8.95, 8.88, 9.30 ppm is assigned to the H^3 proton of the group $-CF_2\underset{|}{C}{=}N{-}NH_2{}^3$ in the bis-hydrazones **4a, 4b** and **4c**, respectively.

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[1] In the reaction, the further 3 mol of hydrazine hydrate are used for binding HF.

Comparison of the ^1H NMR spectral data for the compounds obtained with those for the non-fluorinated analogues show that the chemical shift values for protons H^1 and H^2 in compounds **4a, 4b** and **4c**, and in their analogues are of the same order of magnitude. The only chemical shift of the H^3 protons in the compounds obtained (except compound **10**) is significantly shifted downfield as compared to the non-fluorinated analogues. We can compare the values 8.95, 8.88, 9.30 ppm (for compounds **4a, b, c**) and 6.30, 7.8 ppm (for bis-hydrazones **10** and glyoxal) [8]. Such a difference is likely to be related to the existence of a hydrogen bond between the H^3 protons and the fluorine α-atoms in compounds **4a, 4b** and **4c**.

We should emphasize that the reactivity of unsubstituted bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds (especially their behaviour with respect to oxidizing agents) has not been investigated until now. The preparative method for obtaining such compounds that we have developed makes it possible to undertake such studies.

3. Experimental details

The ^1H and ^{19}F NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer (90 and 84.6 MHz, respectively) with TMS and CF_3COOH as internal standards. IR spectra were recorded using an UR-20 instrument. Mass spectra (EI, 70 eV) were obtained on a 7070 E chromatograph mass spectrometer.

3.1. Preparation of perfluoromethylpentanal hydrazone (2a)

To hydrazine hydrate (11 g, 220 mmol) in 40 ml of CH_3OH was added a solution of perfluoropentanal hydrate (29 g, 109 mmol) in methanol (60 ml). Glacial CH_3COOH (13.2 g, 220 mmol) was then added dropwise with stirring. The homogeneous mixture was stored at room temperature for 24 h. Completion of the reaction was estimated from the disappearance of the signals of the starting compound **1a** in the ^{19}F NMR spectrum of the reaction mixture. The reaction mixture was diluted with water, the organic layer separated, washed with water and dried over calcined $MgSO_4$. Distillation gave hydrazone **2a** (22.8 g, 80%, b.p. 40–42 °C/12 Torr); the b.p. and ^{19}F NMR spectrum of the compound were identical to those for an already known sample [5].

3.2. Preparation of perfluoroheptanal hydrazone (2b)

Hydrazone **2b** (41 g, 83%, b.p. 67–68 °C/10 mmHg) was prepared in a similar manner to that used for **2a** from hydrazine hydrate (18 g, 360 mmol) in 50 ml of CH_3OH and perfluoroheptanal hydrate (50 g, 136 mmol) in 100 ml of CH_3OH. The sample of **2b** obtained was identical to that reported in Ref. [5].

3.3. Preparation of 7-H-dodecafluoroheptanal hydrazone (2c)

Hydrazone **2c** (4.2 g, 70%, b.p. 80–82 °C/1 Torr) was prepared in a similar manner from hydrazine hydrate (1.3 g, 26 mmol) in 5 ml of CH_3OH, 7-*H*-dodecafluoroheptanal hydrate (6 g, 17 mmol) in 5 ml of C_2H_5OH and glacial CH_3COOH (1.5 g, 26 mmol). ^{19}F NMR δ: 38.02 (m, 2F, CF_2); 46.10 (m, 2F, CF_2); 48.20 (m, 4F, $2CF_2$); 55.20 (tm, 2F, CF_2); 62.00 (dm, 2F, CF_2H, $J = 52.5$ Hz) ppm. Analysis: Calc. for $C_7H_4F_{14}N_2$: C, 24.41; H, 1.16; N, 8.13; F, 66.28%. Found: C, 24.61; H, 1.30; N, 8.46; F, 65.94%. MS m/z (species, %): 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).

3.4. Preparation of perfluoropropylglyoxal bis-hydrazone (4a)

Method 1

To a solution of **2a** (15.6 g, 60 mmol) in 50 ml of methanol, hydrazine hydrate (11 g, 220 mmol) in CH_3OH (25 ml) was added and the mixture kept until the reaction was completed (for 20 h). Completion of the reaction was detected from the ^{19}F NMR spectra by the disappearance of signals of the starting compound **1a**. The mixture was diluted with water and the organic layer separated and distilled rapidly in vacuo. Bis-hydrazone **4a** (11.9 g, 78%, b.p. 104–105 °C Torr) was obtained; the b.p. and ^{19}F NMR spectrum of the compound were identical to those of the well-known sample reported in Ref. [2].

Method 2

A mixture of hydrazine hydrate (8 g, 160 mmol), 50 ml of ethanol, CH_3COOH (9.6 g, 160 mmol) and perfluoropentanal hydrate (**1a**) (8 g, 30 mmol) was refluxed fo 3 h. The reaction mixture was then diluted with water and the organic layer separated. Distillation gave a fraction (1.5 g, b.p. 40–103 °C/10 Torr contained mainly monohydrazone **2a**), **4a** (2.3 g, 30%, b.p. 102–104 °C/10 Torr) and a solid residue (2.6 g, 40%) of **5**. The ^{19}F NMR and mass spectra of **5** were identical to those of an already known sample [5].

3.5. Preparation of perfluoropentylglyoxal bis-hydrazone (4b)

Bis-hydrazone **4b** (33 g, 79%, b.p. 106–108 °C/1 Torr) was prepared in a similar manner from **2b** (43.4 g, 120 mmol) and hydrazine hydrate (124 g, 480 mmol). ^{19}F NMR ($CDCl_3$) δ: 3.2 (tm, 3F, CF_3); 34 (tm, 2F, CF_2); 44.7 (m, 4F, $2CF_2$); 48.7 (m, 2F, CF_2) ppm; integral intensity 3:2:4:2. Analysis: Calc. for $C_7H_5F_{11}N_4$: C, 24.01; H, 1.41; N, 15.81; F, 59.04%. Found: C, 24.04; H, 1.33; N, 16.31; F, 59.22%. MS m/z (species, %): 354 $[M]^+$ (45.1); 338 $[M-NH_2]^+$ (12.6); 337 $[M-NH_3]^+$ (9.4); 335 $[M-F]^+$ (5.6); 326 $[M-N_2]^+$ (11.9); 311 $[M-C(H){=}N{-}NH_2]^+$ (6.9); 309

$[M-N_3H_3]^+$ (5.3); 119 $[C_2F_5]^+$ (16.6); 92 $[CF_2\text{–}C{=}N\text{–}NH_2]^+$ (7.9); 87 $[CF{=}CH\text{–}CH{=}N\text{–}NH_2]^+$ (20.1); 85 $[H_2N\text{–}N{=}CH\text{–}C{=}N\text{–}NH_2]^+$ (5.2); 69 $[CF_3]^+$ (46.1); 68 $[C_2H_2N_3]^+$ (12.3); 43 $[CH{=}N\text{–}NH_2]^+$ (100.0); 42 $[C{=}N\text{–}NH_2]^+$ (12.4); 32 $[N_2H_4]^+$ (31.0); 31 $[N_2H_3]^+$ (35.4); 30 $[N_2H_2]^+$ (18.4); 29 $[N_2H]^+$ (13.3); 28 $[N_2]^+$ (14.4); 17 $[NH_3]^+$ (9.1).

*3.6. Preparation of 5-H-decafluoropentylglyoxal bis-hydrazone (**4c**)*

Bis-hydrazone **4c** (2.5 g, 80%, b.p. 137 °C/3 Torr) was prepared in a similar manner from **2c** (3.1 g, 9 mmol) and hydrazine hydrate (2 g, 40 mmol) in 40 ml of methanol. ^{19}F NMR ($CDCl_3$) δ: 39.0 (tm, 2F, CF_2); 46.35 (tm, 2F, CF_2); 47.40 (m, 2F, CF_2); 57.25 (m, 2F, CF_2); 62.15 (dm, 2F, CF_2H, $J=53$ Hz) ppm. MS *m/z* (species, %): 336 $[M]^+$; 320 $[M-NH_2]^+$; 308 $[M-N_2]^+$; 293 $[H(CF_2)_5C{=}N\text{–}NH_2]^+$; 268 $[H(CF_2)_5C{=}NH]^+$; 137 $[CF_2\text{–}CF{=}CH\text{–}CH{=}N\text{–}NH_2]^+$; 118 $[C_3H_2N_3F_2]^+$; 90 $[CF_2\text{–}CN_2]^+$; 87 $[CF{=}CH\text{–}CH{=}N\text{–}NH_2]^+$; 69 $[CF_3]^+$; 51 $[HCF_2]^+$; 43 $[CH{=}N\text{–}NH_2]$.

*3.7. Preparation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethyl-2,3-pentanedione bis-hydrazone (**10**)*

To a mixture of olefin **6** (40 g, 133 mmol) with monoglyme (80 ml), $N_2H_4 \cdot H_2O$ (26 g, 520 mmol) was added dropwise with stirring at 20–25 °C. The reaction mixture was stirred until it was homogeneous and it was then poured into water, the organic layer separated and washed several times with water with shaking. After drying with calcined $MgSO_4$, distillation in vacuo gave the starting olefin **6** (9 g) in a trap (−78 °C) and product **10** (22 g, 73%) was obtained in the form of a colourless liquid, b.p. 89–90 °C/1 Torr, which crystallized immediately, m.p. 85–86 °C (CCl_4). IR (ν_{max} cm^{-1}): 1580, 1640 (s) (C=N); 2940, 3000 (m) (CH); 3245, 3330, 3445 (s) (NH_2). ^{19}F NMR (CCl_4) δ: −14.7, −13.8 (m, 3F, CF_3); −11.3 [dq, 6F, $(CF_3)_2CH$, $J=10$ Hz] ppm. MS *m/z* (species, %): 304 $[M]^+$ (19.6); 228 $[M-NH_2]^+$ (32.7); 287 $[M-NH_3]^+$ (15.1); 285 $[M-F]^+$ (13.5); 268 $[M-HF, NH_2]^+$ (15.5); 259 $[M-N_3H_3]^+$ (14.7); 256 $[M-HF, N_2]^+$ (37.4); 248 $[M-2N_2]^+$ (22.5); 193 $[(CF_3)_2CH\text{–}C{=}N\text{–}NH_2]^+$ (66.7); 111 $[CF_3\text{–}C{=}N\text{–}NH_2]^+$ (55.6); 69 $[CF_3]^+$ (100); 42 $[C{=}N\text{–}NH_2]^+$ (50.0). Analysis: Calc. for $C_6H_5F_9N_4$: C, 23.68; H, 1.64; N, 18.42%. Found: C, 23.59; H, 1.66; N, 18.67%.

Acknowledgements

This work was supported by the International Science Foundation (Grants No. NNDL000 and DL 300) and the Russian Foundation for Basic Research (Project No. 94-03-08548).

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