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Polyfluoroalkyl-substituted 1-amino-1,2,3-triazoles

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

Institute of Organoelement Chemistry, Russian Academy of Sciences, 28, ul. Vavilova, 117813 Moscow, Russia

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Abstract

New polyfluorinated 1-amino-1,2,3-triazoles were obtained by oxidation of the bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds with sulphuryl chloride, bromine or selenium dioxide in an aprotic solvent.

Keywords: Oxidation; Bromine; Sulphuryl chloride; Selenium dioxide; Bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds; 1-Amino-1,2,3-triazoles; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Polyfluorinated 1-amino-1,2,3-triazoles may be of interest for industrial purposes and as biologically active substances with a wide spectrum of effect. However, until now these compounds have not been available. Non-fluorinated analogues of such compounds were obtained by a two-step method in small yield by treatment of bis-tosylhydrazones with sodium or potassium methylate [1]. The alternative method used for 1-amino-1,2,3-triazoles is the oxidation of *N,N*-unsaturated bis-hydrazones; but this method provides successful results only in the case of the oxidation of hydrazones of cyclic α-diketones [2].

The formation of 1-amino-1,2,3-triazoles is only assumed in the oxidation of non-fluorinated bis-hydrazones of aliphatic α-dicarbonyl compounds; in this reaction a dialkylacetylene was isolated as the sole product [3].

The oxidation of bis-hydrazones of aliphatic polyfluorinated α-dicarbonyl compounds had not been investigated before our studies.

2. Results and discussion

Recently, we have shown that the oxidation of the bis-hydrazone **1** with bromine in water yields the α-diazoketone $[(CF_3)_2CH–C(N_2)–C(O)–CF_3]$, which is the product of the hydrolysis of one hydrazone group and the oxidation of the other hydrazone group in the starting compound [4].

In the present work, we studied the oxidation of bis-hydrazones of polyfluorinated α-dicarbonyl compounds with bromine, sulphuryl chloride and selenium dioxide under anhydrous conditions in aprotic solvents.

It turned out that oxidation of the bis-hydrazone **1** (see Ref. [4]) with bromine in CCl_4 led to 1-amino-4-(1,1,1,3,3,3-hexafluoroisopropyl)-5-trifluoromethyl-1,2,3-triazole (**3a**) in 70% yield (Scheme 1). The same product was isolated in ca. 80% yield when sulphuryl chloride was used as the oxidizing agent (see Preliminary Communication [5]).

One hydrazone group in the starting compound is probably oxidized first and the possible isomers formed (**2a** and **2b**) are converted to 1-amino-1,2,3-triazole **3a** and **3b**, the products of the intramolecular attack at the diazo group by the second hydrazone group. It was shown that the compound obtained existed in the form of one isomer using chromatography/mass spectrometry. X-Ray diffraction analysis confirmed the structure of 1,2,3-triazole **3a** (Fig. 1).

We obtained 1-amino-5-perfluoropentyl- (**5a**) and -5-*H*-decafluoropentyl-1,2,3-triazoles (**5b**) in high yield by oxidation of the bis-hydrazones of the polyfluoroalkyl-substituted glyoxals (**4a** and **4b**) with SeO_2 in CH_2Cl_2 (Scheme 2). (The synthesis of **4a** and **4b** is reported in Ref. [6].)

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)

* Corresponding author.

[1] Earlier in the Preliminary Communication [5], the structure of 1-amino-1,2,3-triazole (**3b**) was assigned to this compound.

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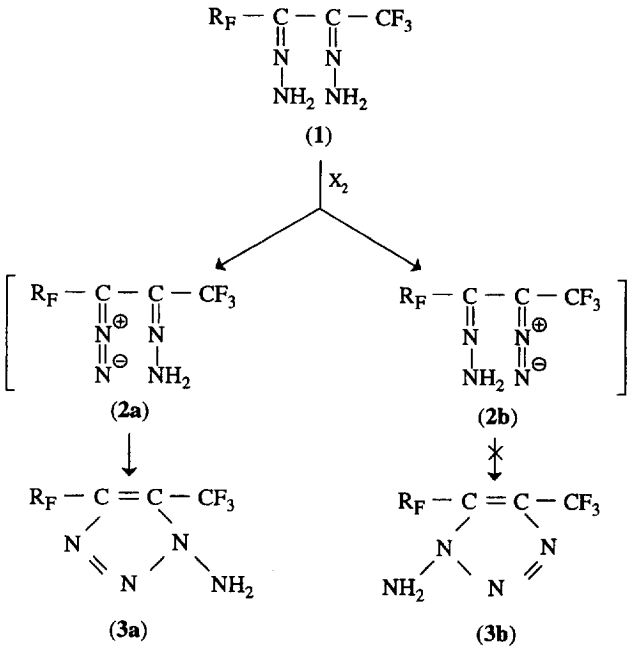


Scheme 1. $R_F = (CF_3)_2CH$; $X = Br_2$, SO_2Cl_2.

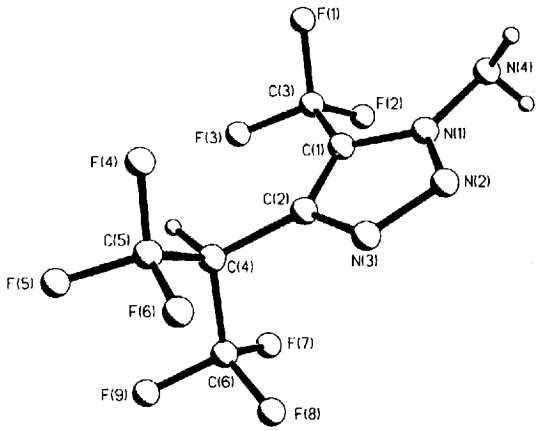
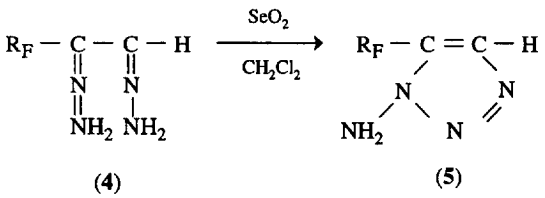


Fig. 1. Molecular structure of compound **3a** in the crystal state.



Scheme 2. [$R_F = CF_3(CF_2)-$ (**4a**, **5a**); $HCF_2(CF_2)-$ (**4b**, **5b**)].

with TMS and CF_3COOH used as internal standards. IR spectra were recorded using a UR-20 spectrophotometer. Mass spectra were obtained on a 7070 E instrument (70 eV).

3.1. Preparation of 1-amino-4-(1,1,1,3,3,3-hexafluoroisopropyl)-5-trifluoromethyl-1,2,3-triazole (3a)

Procedure 1

To a solution of the bis-hydrazone **1** (29 g, 96 mmol) in dry CH_2Cl_2 (60 ml), freshly distilled SO_2Cl_2 (26 g, 193 mmol) was added dropwise at 20–25 °C with stirring. The solution was stirred until the liberation of HCl was complete, then unreacted SO_2Cl_2 was distilled off into a trap (−78 °C) at 20–25 °C/5 mmHg, and the solid residue was recrystallized from CCl_4. Product **3a** (25 g, 82%, m.p. 90–92 °C) was obtained. IR (ν_{max}, cm^{-1}): 1370–1380 (s) (N=N); 1480–1500 (m) (N=N); 1600–1630 (m) (C=C); 2930, 3010 (w) (CH); 3280 (m); 3370 (s) (NH_2). ^1H NMR ($CDCl_3$) δ: 5.8 (br.s, 2H, NH_2); 3.4 [hpt, 1H, $CH(CF_3)$, $J = 10$ Hz] ppm. ^{19}F NMR ($CDCl_3$) δ: −18.2 (s, 3F, CF_3); −12.7 [d., 6F, $(CF_3)CH$, $J = 10$ Hz] ppm. Analysis: Calc. for $C_6H_3F_9N_4$: C, 23.84; H, 0.99; F, 56.62; N, 18.64%. Found: C, 23.71; H, 1.14; F, 55.80; N, 18.98%. MS (*m/z*, species, %): 303 $(M+1)^+$(2.0); 288 $(M-F)^+$(1.0); 274 $(M-N_2)^+$(14.7); 255 $(M-N_2-F)^+$(2.9); 235 $(M-N_2-HF,F)^+$(4.4); 225 $(M-F,N_4,H_2)^+$(22.4); 205 $(M-N_2-CF_3)^+$(6.1); 185 $(M-N_2, CF_3, HF)^+$)(12.4); 163 $[(CF_3)_2CH-C=]^+$(1.4); 157 $(C_4F_3N_3)^+$(9.7); 137 $(C_3H_2N_2F_3)^+$(5.1); 135 $(C_3N_3F_3)^+$(3.3); 111 $(CF_3-C=N-NH_2)^+$(1.5); 93 $(CF_3-C=C-)^+$(6.5); 82 $(C_2H_2N_4)^+$(1.2); 69 $(CF_3)^+$(100); 66 $(C_2N_3)^+$(6.6); 42 $(C=N-NH_2)^+$(2.8); 32 $(N_2H_4)^+$; 28 $(N_2)^+$.

Procedure 2

To the bis-hydrazone **1** (0.5 g, 1.6 mmol) in 5 ml of CCl_4, Br_2 (4 g, 3.7 mmol) in 10 ml of CCl_4 was added dropwise with stirring. The solution was stirred until the liberation of HBr was complete, then the solvent and excess Br_2 were removed using a rotory evaporator. The solid residue was recrystallized from CCl_4 to give product **3a** (0.4 g, 77%) whose ^1H, ^{19}F NMR and mass spectra were identical to those for the already known sample.

3.1.1. Crystal structure determination of 3a

The single-crystal X-ray diffraction data for compound **3a** were collected at −120 °C on an automated Siemens P3/PC 4-circled diffractometer with graphite-monochromated Mo Kα radiation, $\theta/2\theta$ scanning, $2\theta > 60°$. Crystal system, rhombic; at −120 °C: $a = 13.598(8)$ Å, $b = 11.915(6)$ Å, $c = 6.585(5)$ Å, $V = 1066.9(12)$ Å^3, $M = 302.12$, space group $Pca21$, $Z = 4$, $d_{calc} = 1.881$ g cm^{-3}, $\mu = 0.230$ mm^{-1}. The structure was solved and refined by least-squares full-matrix methods in anisotropic approximation.

3.2. Preparation of 1-amino-5-perfluoropentyl-1,2,3-triazole (5a)

A mixture of SeO_2 (2 g, 18 mmol) in 20 ml of CH_2Cl_2 and the bis-hydrazone **4a** (2 g, 5.7 mmol) in 10 ml of CH_2Cl_2 was stirred at room temperature for 3 h. The solution was then filtered though a paper filter, the filtrate evaporated in vacuo, and the residue crystallized from CCl_4 to yield 1.4 g of **5a** (70%, m.p. 82–83 °C). IR (ν_{max}, cm^{-1}): 1300, 1330, 1380 (s) (N=N); 1630 (m), 3220, 3340 (s) (NH_2). Analysis: Calc. for $C_7F_{11}H_3N_4$: C, 23.95; H, 0.81; N, 15.75%. Found: C, 23.86; H, 0.85; N, 15.91%. MS (*m/z*, species, %): 353 $(M+1)^+$(0.2); 352 $(M)^+$(1.3); 333 $(M-F)^+$(5.2);

324 $(M-N_2)^+$ (3.4); 305 $(M-F,N_2)^+$ (3.6); 285 (M−F, HF, N_2)$^+$ (3.8); 275 (M−F, HF, N_2H_2)$^+$ (4.7); 169 $(C_3F_7)^+$ (2.1); 119 $(C_2F_5)^+$ (7.7); 105 $(C_3H_3F_2N_2)^+$ (15.3); 100 $(C_2F_4)^+$ (2.8); 69 $(CF_3)^+$ (30.3); 57 $(N_4H)^+$ (3.9); 55 $(C_2H_3N_2)^+$ (6.9); 51 $(C_2F_4)^+$ (6.9); 43 $(CH{=}N{-}NH_2)^+$ (6.2); 31 $(N_2H_3)^+$ (3.7); 30 $(N_2H_2)^+$ (100.0); 29 $(N_2H)^+$ (11.3); 28 $(N_2)^+$ (4.7). ^{1}H NMR ($CDCl_3$) δ: 4.85 (br.s, 2H, NH_2); 7.95 (s, 1H, CH) ppm. ^{19}F NMR ($CDCl_3$) δ: 3.00 (m, 3F, CF_3); 32.00 (m, 2F, CF_2); 44.50 (m, 2F, CF_2); 45.20 (m, 2F, CF_2); 48.50 (m, 2F, CF_2) ppm.

*3.3. Preparation of 1-amino-5-H-decafluoropentyl-1,2,3-triazole (**5b**)*

This was obtained in a similar manner from SeO_2 (4 g, 36 mmol) in 20 ml of dry CH_2Cl_2 and the bis-hydrazone **4b** (4 g, 12 mmol) in 20 ml of CH_2Cl_2. Recrystallization of the crude product gave **5b** (3.2 g, 80%, m.p. 69–70 °C). Analysis: Calc. for $C_7H_4F_{10}N_4$: C, 24.90; H, 1.06; N, 16.65%. Found: C, 25.15; H, 1.20; N, 16.76%. MS (*m/z*, species, %): 334 $(M)^+$ (1.9); 315 $(M-F)^+$ (3.8); 306 $(M-N_2)^+$ (3.2); 287 $(M-N_2-F)^+$ (3.1); 257 $(M-N_4H_2, F)^+$ (5.3); 227 $(M-N_4H_2, F, 2HF)^+$ (1.1); 169 $(C_3F_7)^+$ (1.2); 151 $[H(CF_2)_3]^+$ (1.6); 101 $[H(CF_2)_2]^+$ (8.4); 100 $[(CF_2)_2]^+$ (3.1); 75 $(CF_2{-}C{=}CH)^+$ (17.2); 69 $(CF_3)^+$ (22.3); 58 $(N_4H_2)^+$ (1.1); 57 $(N_4H)^+$ (4.4); 56 $(N_4)^+$ (1.6); 55 $(C_2H_3N_2)^+$ (8.2); 51 $(CF_2H)^+$ (35.2); 43 $(CH{=}N{-}NH_2)^+$ (23.5); 31 $(N_2H_3)^+$ (5.6); 30 $(N_2H_2)^+$ (100.0); 29 $(N_2H)^+$ (14.4); 28 $(N_2)^+$ (5.0); 17 $(NH_3)^+$ (2.2). ^{1}H NMR [$(CD_3)_2C{=}O$] δ: 8.55 (br.s, 1H, CH=N); 6.85 (tt, 1H, HCF_2, J(H–CF_2) = 50.5 Hz); 3.00 (br.s, 2H, NH_2) ppm. ^{19}F NMR [$(CD_3)_2C{=}O$] δ: +31.00 (m, 2F, CF_2); +44.00 (m, 4F, $2CF_2$); +53.50 (m, 2F, CF_2); +60.50 [dm, 2F, CF_2, $J(CF_2{-}H)$ = 50.5] ppm.

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