Polyfluorinated hydrazones in organic synthesis
2.* Oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone. Synthesis and structure of 1-amino-5-trifluoromethyl-4-(1,1,1,3,3,3-hexafluoroisopropyl)-1,2,3-triazole

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Oxidation of *N,N'*-unsubstituted 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone with sulfuryl chloride or bromine in CCl_4 gives 1-amino-5-trifluoromethyl-4-(1,1,1,3,3,3-hexafluoroisopropyl)-1,2,3-triazole in high yield. Its structure has been confirmed by X-ray structural analysis.

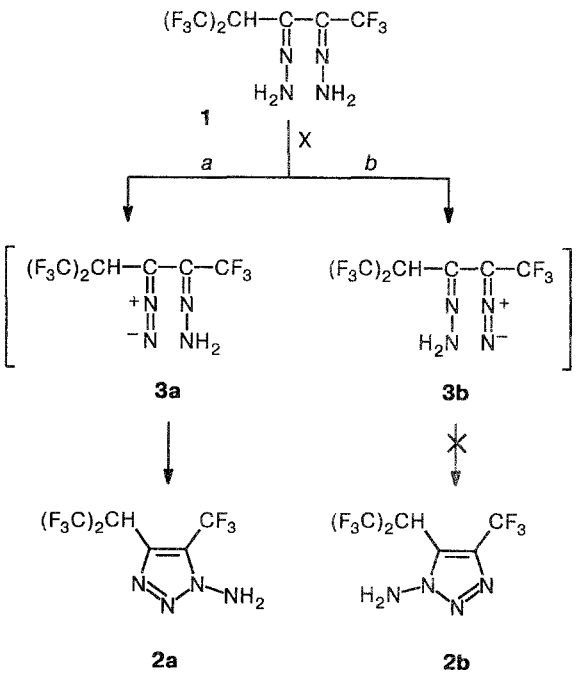
Key words: oxidation, X-ray structural analysis, bromine, sulfuryl chloride, 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone, 1-amino-5-trifluoromethyl-4-(1,1,1,3,3,3-hexafluoroisopropyl)-1,2,3-triazole.

Previously, we have demonstrated that oxidation of bishydrazone (**1**) with bromine in water affords α-diazoketone, the product of hydrolysis of one hydrazone group and of oxidation of the second hydrazone group.[1] As part of continuing studies of the effect of different factors on the process of oxidation of *N,N'*-unsubstituted hydrazones of polyfluorinated aliphatic α-diketones, in this work we have studied oxidation of bishydrazone **1** with bromine under anhydrous conditions and with sulfuryl chloride in an aprotic solvent.

It has been found that oxidation of bishydrazone **1** (see Ref. 1 for its preparation) with bromine in CCl_4 gives 1-amino-5-trifluoromethyl-4-(1,1,1,3,3,3-hexafluoroisopropyl)-1,2,3-triazole (**2a**) in ~70 % yield. This product was also isolated in ~80 % yield when sulfuryl chloride was used as an oxidant (Scheme 1).

The scheme of formation of compound **2a** can be conceived as the oxidation of the hydrazone group at the C(3) atom of compound **1** (pathway *a*) with its conversion to an intermediate diazo compound (**3a**) followed by cyclization. The second isomer (**2b**), which could be obtained if the hydrazone group at the C(2) atom of compound **1** was oxidized (pathway *b*), was not formed

Scheme 1



X = Br_2; SO_2Cl_2

* For Part 1 see Ref. 1.
† Deceased.

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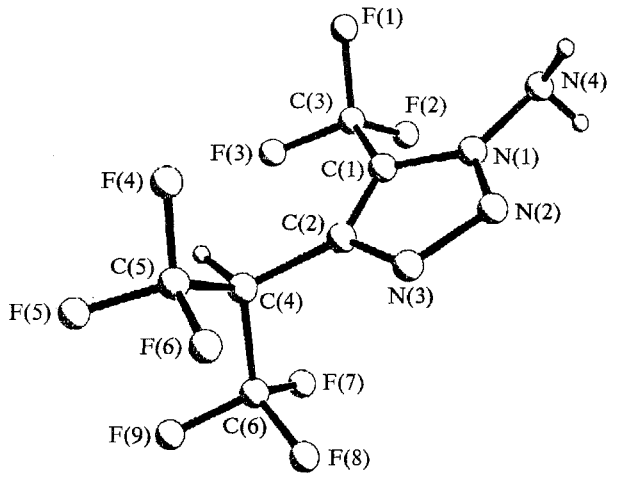

Fig. 1. Overall view of molecule **2a** in the crystal.

at all, which is confirmed by chromatomass spectrometry. The structure of 1-amino-1,2,3-triazole **2a** (Fig. 1) has been unambiguously established by X-ray structural analysis.*

Note that 1-amino-1,2,3-triazoles were not isolated previously upon oxidation of *N,N'*-unsubstituted bishydrazones of aliphatic α-diketones; however, the formation of these compounds (as intermediates) in this process was expected.[3]

Experimental

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

1-Amino-5-trifluoromethyl-4-(1,1,1,3,3,3-hexafluoroisopropyl)-1,2,3-triazole (2a). *A.* Freshly distilled SO_2Cl_2 (26 g, 193 mmol) was added dropwise to a solution of bishydrazone **1** (29 g, 96 mmol) in dry CH_2Cl_2 (60 mL) with stirring at 20—25 °C. The solution was stirred until evolution of hydrogen chloride ceased (3 h), and then excess SO_2Cl_2 was distilled off at 20—25 °C (5 Torr) into a trap at −78 °C. The solid residue was recrystallized from CCl_4 to give compound **2a**, m.p. 90—92 °C, in a yield of 25 g (82 %). IR, ν/cm^{-1}: 1370—1380 s (N=N); 1480—1500 m (N=N); 1600—1630 m (C=C); 2930 and 3010 w (CH); 3280 m, 3370 s (NH_2). ^1H NMR ($CDCl_3$), δ: 5.8 (br.s, 2 H, NH_2); 3.4 (hept, 1 H, $CH(CF_3)_2$, J = 10 Hz). ^{19}F NMR ($CDCl_3$), δ: −18.2 (s, 3 F, CF_3); −12.7 (d, 6 F, $(CF_3)_2CH$, J = 10 Hz). Found (%): C, 23.71; H, 1.14; F, 55.80; N, 18.98. $C_6H_3F_9N_4$. Calculated (%): C, 23.84; H, 0.99; F, 56.62; N, 18.64. Mass spectrum, m/z (I (%)): 303 $[M+1]^+$ (2.0), 283 $[M-F]^+$ (1.0), 274 $[M-N_2]^+$ (14.7), 255 $[M-N_2-F]^+$ (2.9), 235 $[M-N_2HF,F]^+$ (4.4), 225 $[M-F,N_4,H_2]^+$ (22.4), 205 $[M-N_2CF_3]^+$ (6.1), 185

* Previously (see preliminary communication),[2] the structure of 1-amino-1,2,3-triazole **2b** was assigned to the compound obtained.

Table 1. Bond lengths (d) and bond angles (φ) in the structure of **2a**

Bond	d/Å	Bond	d/Å
F(1)—C(3)	1.333(5)	N(1)—N(2)	1.345(6)
F(2)—C(3)	1.315(6)	N(1)—C(1)	1.354(6)
F(3)—C(3)	1.338(6)	N(1)—N(4)	1.398(5)
F(4)—C(5)	1.326(8)	N(2)—N(3)	1.327(6)
F(5)—C(5)	1.345(7)	N(3)—C(2)	1.347(6)
F(6)—C(5)	1.331(8)	C(1)—C(2)	1.379(6)
F(7)—C(6)	1.336(8)	C(1)—C(3)	1.476(7)
F(8)—C(6)	1.304(8)	C(2)—C(4)	1.515(6)
F(9)—C(6)	1.329(6)	C(4)—C(5)	1.501(8)
C(4)—C(6)	1.521(7)		

Angle	φ/deg	Angle	φ/deg
N(2)—N(1)—C(1)	112.1(3)	F(3)—C(3)—C(1)	110.5(4)
N(2)—N(1)—N(4)	122.4(4)	C(5)—C(4)—C(2)	111.5(4)
C(1)—N(1)—N(4)	125.6(4)	C(5)—C(4)—C(6)	113.4(4)
N(3)—N(2)—N(1)	106.3(4)	C(2)—C(4)—C(6)	111.1(4)
N(2)—N(3)—C(2)	108.9(4)	F(4)—C(5)—F(6)	106.9(6)
N(1)—C(1)—C(2)	103.2(4)	F(4)—C(5)—F(5)	106.2(5)
N(1)—C(1)—C(3)	122.7(4)	F(6)—C(5)—F(5)	107.7(5)
C(2)—C(1)—C(3)	134.1(4)	F(4)—C(5)—C(4)	110.4(5)
N(3)—C(2)—C(1)	109.5(4)	F(6)—C(5)—C(4)	113.9(5)
N(3)—C(2)—C(4)	121.2(4)	F(5)—C(5)—C(4)	111.3(5)
C(1)—C(2)—C(4)	129.2(4)	F(8)—C(6)—F(9)	107.9(5)
F(2)—C(3)—F(1)	106.5(4)	F(8)—C(6)—F(7)	106.6(5)
F(2)—C(3)—F(3)	107.9(4)	F(9)—C(6)—F(7)	107.8(6)
F(1)—C(3)—F(3)	106.6(4)	F(8)—C(6)—C(4)	113.4(5)
F(2)—C(3)—C(1)	112.3(4)	F(9)—C(6)—C(4)	112.1(4)
F(1)—C(3)—C(1)	112.8(4)	F(7)—C(6)—C(4)	108.8(5)

Table 2. Atomic coordinates of nonhydrogen atoms (×10^4) in the structure of **2a** and equivalent thermal parameters (U_{eq})

Atom	x	y	z	$U_{eq} \cdot 10^3$/Å^2
F(1)	−0.2452(2)	−0.1935(3)	−0.4243(5)	0.0451(8)
F(2)	−0.1383(3)	−0.1118(4)	−0.6063(5)	0.0538(9)
F(3)	−0.1163(3)	−0.2831(3)	−0.5172(6)	0.0583(10)
F(4)	−0.0754(4)	−0.3791(3)	0.0836(9)	0.084(2)
F(5)	0.0455(3)	−0.4821(3)	−0.0074(7)	0.0701(13)
F(6)	0.0700(4)	−0.3338(4)	0.1746(7)	0.084(2)
F(7)	0.1291(3)	−0.2433(4)	−0.4261(8)	0.0775(14)
F(8)	0.1861(2)	−0.2364(3)	−0.1273(10)	0.081(2)
F(9)	0.1736(2)	−0.3950(3)	−0.2740(8)	0.0625(11)
N(1)	−0.1100(2)	−0.0452(3)	−0.1832(7)	0.0250(7)
N(2)	−0.0518(3)	−0.0300(3)	−0.0203(7)	0.0297(8)
N(3)	0.0016(3)	−0.1226(3)	−0.0022(7)	0.0292(8)
N(4)	−0.1761(3)	0.0367(3)	−0.2501(7)	0.0313(9)
C(1)	−0.0953(3)	−0.1465(4)	−0.2713(7)	0.0245(9)
C(2)	−0.0240(3)	−0.1947(4)	−0.1508(7)	0.0240(9)
C(3)	−0.1488(3)	−0.1828(4)	−0.4550(7)	0.0289(9)
C(4)	0.0254(3)	−0.3081(4)	−0.1711(8)	0.0277(9)
C(5)	0.0173(5)	−0.3750(5)	0.0214(10)	0.0486(14)
C(6)	0.1304(4)	−0.2961(4)	−0.2472(11)	0.0444(14)

Table 3. Atomic coordinates of hydrogen atoms ($\times 10^2$) in the structure of **2a** and isotropic thermal parameters (U_{iso})

Atom	x	y	z	$U_{iso} \cdot 10^2/Å^2$
H(4)	−0.0071(36)	−0.3603(46)	−0.2792(96)	0.029(13)
H(4A)	−0.1406(43)	0.0881(52)	−0.2795(102)	0.032(14)
H(4B)	−0.2082(40)	0.0585(47)	−0.1226(104)	0.035(15)

$[M-N_2,CF_3,HF]^+$ (12.4), 163 $[(CF_3)_2CHC]^+$ (1.4), 147 $[C_4F_3N_3]^+$ (9.7), 137 $[C_3H_2N_3F_3]^+$ (5.1), 135 $[C_3N_3F_3]^+$ (3.3), 111 $[CF_3C{=}NNH_2]^+$ (1.5), 93 $[CF_3C{=}C]^+$ (6.5), 82 $[C_2H_2N_4]^+$ (1.2), 69 $[CF_3]^+$ (100), 66 $[C_2N_3]^+$ (6.6), 42 $[C{=}NNH_2]^+$ (2.8), 32 $[N_2H_4]^+$, 28 $[N_2]^+$.

B. A solution of Br_2 (4 g, 3.7 mmol) in 10 mL of CCl_4 was added dropwise to a solution of bishydrazone **1** (0.5 g, 1.6 mmol) in 5 mL of CCl_4 with stirring. The solution was stirred until evolution of HBr ceased. The solvent and excess Br_2 were removed on a rotary evaporator, and the solid residue was recrystallized from CCl_4 to give compound **2a** in a yield of 0.4 g (77 %); according to ^1H and ^{19}F NMR and mass spectra, this compound is identical to that described above.

X-ray diffraction study of compound **2a** was carried out on an automated four-circle Siemens P3/PC diffractometer at −120 °C (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, 2θ > 60°). Crystals are orthorhombic, at −120 °C: a = 13.598(8), b = 11.915(6), c = 6.585(5) Å, V = 1066.9(12) Å^3. Mol. wt. 302.12, space group *Pca*21, Z = 4, d_{calc} = 1.881 mg cm^{-3}, μ = 0.230 mm^{-1}. The structure was solved and refined anisotropically by the full-matrix least-squares method.

Hydrogen atoms were located from difference electron density syntheses; all these atoms were included in the final refinement with isotropic temperature factors. Calculations were performed using 2519 measured reflections. The final R factors are: R_1 = 0.0689 using 1732 independent reflections with $I > 2\sigma(I)$, wR_1 = 0.1721 using a total of 2519 measured reflections, GOF 1.08. All calculations were performed on an IBM-PC/AT computer using the SHELXL program package (Version 3). Bond lengths and bond angles are listed in Table 1; atomic coordinates of nonhydrogen and hydrogen atoms and their equivalent isotropic thermal parameters are given in Tables 2 and 3.

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