### Letters to the Editor

# A new reaction of intramolecular cyclization in a series of aliphatic polynitro compounds

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We discovered a new reaction of intramolecular cyclization in a series of aliphatic polynitro compounds, in particular, of the dipotassium salt of 1,1,5,5-tetranitro-3-oxapentane prepared by deformylation of 2,2,6,6-tetranitro-4-oxaheptane-1,7-diol<sup>1</sup> by the action of potassium hydroxide. The cyclization affords a novel heterocyclic compound, 5,5-dinitro-4-acetoxy-5,6-dihydro-2*H*-oxazine *N*-oxide (1), which contains nitro groups, an acetate group, and an *N*-oxide group in the oxazine ring.

Compound 1 is formed in 59 % yield as a white powder when the dipotassium salt of 1,1,5,5-tetranitro-3-oxapentane is treated with aqueous acetic acid at room temperature.

$$\begin{tabular}{l} $\stackrel{+}{\bar{C}}(NO_2)_2CH_2OCH_2\bar{C}(NO_2)_2K^+$} & $\stackrel{AcOH, H_2O}{\longrightarrow} & O_2N & C & O_2N & C$$

During the reaction, compound 1 remains in solution and is isolated by diluting the reaction mixture with water. After recrystallization from CHCl<sub>3</sub> compound 1 is a stable crystalline solid, m.p. 100-101 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, TMS)  $\delta$ : 2.22 (s, 3 H, Me); 4.63 (br. s, 2 H, CH<sub>2</sub>); 5.0 (br. s, 2 H, CH<sub>2</sub>). After cooling, the spectrum transforms into an AB pattern,  $\Delta\delta \approx 55$  Hz ( $\delta = 5.0$ );  $\Delta\delta = 10$  Hz ( $\delta = 4.63$ ).

IR (acetone),  $v/cm^{-1}$ : 1760 (C=O); 1602, 1588, 1316 [C(NO<sub>2</sub>)<sub>2</sub>]; 1293 (N<sup>+</sup>-O<sup>-</sup>); 1115 (C-O-C).

Crystals of 1 with M = 249.15 are rhombic, a = 23.413 (8); b = 14.285 (5), c = 5.900 (6) Å, V = 1973.7 Å<sup>3</sup>, d = 1.676 g cm<sup>-3</sup>,  $\lambda = 0.7107$  Å, space group Pcab, Z = 8. The structure was solved by the direct method on a personal computer using the SHELX-86 set of programs. The coordinates of the atoms were refined in the full-matrix approximation to R = 0.051. The coordinates of the hydrogen atoms were determined directly in the electron density synthesis.<sup>2</sup>

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 4-03-08680).

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Received May 4, 1994; in revised form August 26, 1994

# Formation of 1-amino-1,2,3-triazole in the oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione dihydrazone

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Dihydrazones of aliphatic  $\alpha$ -diketones are known to be converted into dialkylacetylenes *via* the intermediate formation of aminotriazole, which then entirely loses hydrogen and nitrogen.

Unexpectedly, it turned out that oxidation of dihydrazone of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione (1) (see Ref. 2) with sulfuryl chloride under mild conditions affords 1-amino-4-trifluoromethyl5-(1,1,1,3,3,3-hexafluoro-2-propyl)-1,2,3-triazole (2) in a yield of ~80 % (Scheme 1).

#### Scheme 1

 $SO_2Cl_2$  has not been used hitherto for the oxidation of aliphatic  $\alpha$ -diketone dihydrazones.

Polyfluoroalkyl substituted 1-amino-1,2,3-triazoles have not been described.

Compound **2**. m.p. 90—92 °C (from CCl<sub>4</sub>). IR,  $v/cm^{-1}$ : 1370—1380 s (N=N); 1480—1500 m (N=N); 1600—1630 m, 2930 and 3010 w (CH); 3280 m, 3370 s (NH<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 5.8 (s, 2 H, NH<sub>2</sub>); 9.4 (hept, 1 H, J=10 Hz, CH(CF<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>),  $\delta$ : -18.2 (s, 3 F, CF<sub>3</sub>); -12.7 (d, 6 F, J=10 Hz, (CF<sub>3</sub>)<sub>2</sub>CH). Found (%): C, 23.71; H, 1.14; F, 55.80; N, 18.98. C<sub>6</sub>H<sub>3</sub>F<sub>9</sub>N<sub>4</sub>. Calculated (%): C, 23.84; H, 0.99; F, 56.62; N, 18.64. MS, m/z: 303 [M+1 H]<sup>+</sup>; 274 [M-N<sub>2</sub>]<sup>+</sup>; 255 [M-N<sub>2</sub>, F]<sup>+</sup>; 235 [M-N<sub>2</sub>, F, HF]<sup>+</sup>; 225 [M-F, N<sub>2</sub>H<sub>2</sub>]<sup>+</sup>; 157 [M-3 F, N<sub>4</sub>H<sub>2</sub>]<sup>+</sup>; 185 [M-2 HF, F, N<sub>2</sub>H<sub>2</sub>]<sup>+</sup>; 157 [M-3 F, N<sub>4</sub>H<sub>2</sub>]<sup>+</sup>; 137 [M-N<sub>2</sub>]<sup>+</sup>; 113 [C<sub>3</sub>F<sub>4</sub>H]<sup>+</sup>; 93 [C<sub>3</sub>F<sub>3</sub>]<sup>+</sup>; 69 [CF<sub>3</sub>]<sup>+</sup>; 30 [H<sub>2</sub>N-N]<sup>+</sup>.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 94-03-08548).

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Received June 27, 1994