Novel transformations of nitraminodiol diacetates

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A novel scission reaction of nitraminodiol diacetates of the formula $AcO[CH_2N(NO_2)]_xCH_2OAc$ (x = 1-4) in concentrated sulfuric acid to form formaldehyde, nitramide, and 2-nitro-2-azapropane-1,3-diol disulfate was found.

Key words: nitraminodiol diacetates, 2,4,6-trinitro-2,4,6-triazaheptane-1,7-diol diacetate, 2,2,2-trinitroethanol, trinitromethane and its potassium salt, 1,1,1,7,7,7-hexanitro-3,5-dioxaheptane, 1,1,1,5,5,5-hexanitro-3-azapentane, nitramide.

Nitraminodiol diacetates are available and widely used reagents for the synthesis of N-nitroamines.¹⁻⁴ It is known that under the action of acids these compounds undergo numerous reactions of nucleophilic substitution of the acetate group, resulting in yields of 70 to 85 % (Scheme 1).⁵⁻⁷

Scheme 1



We found a novel direction of reaction of nitraminodiol diacetates in acidic media. For example, 1,1,1,7,7,7-hexanitro-3,5-dioxaheptane (2) was obtained from 2,4,6-trinitro-2,4,6-triazaheptane-1,7-diol diacetate (1) under the action of 2,2,2-trinitroethanol in H_2SO_4 at 14-20 °C (yield 86-88 %).

$$1 \xrightarrow[H_2SO_4, H_2O]{C(NO_2)_3CH_2(OCH_2)_2C(NO_2)_3} C(NO_2)_3 C(NO_2) C(NO_2)_3 C(NO$$

A sole product, 1,1,1,5,5,5-hexanitro-3-azapentane (3), was isolated when compound 1 was treated with

trinitromethane or its potassium salt under the same conditions (yield 28-30 %).

$$1 \xrightarrow{H \subseteq NO_{2}}_{H_{2}SO_{4}, H_{2}O} \xrightarrow{f \in (NO_{2})_{3}} C(NO_{2})_{3}CH_{2}NHCH_{2}C(NO_{2})_{3} \xrightarrow{(3)}$$

1,1,1,3,5,5,5-Heptanitro-3-azapentane (4) (yield 88 %, m.p. 95-96 °C, $d_4^{20} = 1.93$) was obtained by nitration of compound 3.

$$3 \xrightarrow{\text{HNO}_3 + \text{H}_2\text{SO}_4} C(\text{NO}_2)_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3 \qquad (4)$$

Compositions and structures of products 2-4 were confirmed by elemental analysis and ¹H NMR spectra.

In the known cases, 5-7 the acetate group is also substituted in the presence of acid, and nitraminocarbonium cations generated are stabilized due to the addition of anions, which are present in the medium.

As in our case, the process becomes more difficult when the amount of H_2SO_4 increases: 50 to 60 moles of H_2SO_4 is taken per mole of compound 1. In this case, the scission of compound 1 via reaction (5)

$$1 + 2H_2SO_4 \longrightarrow 2CH_2(OSO_3H)_2 + 2NH_2NO_2 +$$

$$5 \qquad 6$$

$$+ HOSOCH_2NCH_2OSOH \qquad (5)$$

$$+ HOSOCH_2NCH_2OSOH \qquad (5)$$

$$-7$$

should be assumed along with the protonation of oxygen atoms of the acetate groups.

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It is known⁸ that the reaction of 2,2,2-trinitroethanol with formaldehyde in concentrated H_2SO_4 results in the formation of formal 2 (yield ~90 %), which can be easily isolated by crystallization from CCl₄. In other words, 2,2,2-trinitroethanol in concentrated H_2SO_4 is a convenient reagent for determination of formaldehyde.

Thus, the preparation of formal 2 by treatment of compound 1 with excess of concentrated H_2SO_4 in the presence of 2,2,2-trinitroethanol makes it possible to consider formaldehyde (evidently, in the form of methylene glycol disulfate) to be one of the main products of acidic scission of diacetate 1. The yield of formal 2 (calculated per reacted 2,2,2-trinitroethanol) is close to the quantitative one, which confirms the formation of two moles of formaldehyde from diacetate 1 (reaction (5)).

The reaction is accompanied by ample gas evolution, due likely to the decomposition of nitramide 6 in the reaction

$$NH_2NO_2 \rightarrow N_2O + H_2O. \tag{6}$$

Nitrous oxide evolved is quantitatively determined by volumetry and identified by the IR spectrum. The yield of N_2O is 92 to 94 % (calculated on the basis of reaction (6)).

The third product of the acidic scission of 1, disulfate 7, was identified by its Mannich condensation with trinitromethane and transformation to compound 3:

$$7 \quad \frac{HC(NO_2)_3}{H^+} \quad 3 \tag{7}$$

When the reaction mixture is diluted by a great amount of water, reaction product 3 precipitates.

It is experimentally established that acidic scission in concentrated H_2SO_4 is general for nitraminodiol diacetates of the general formula $AcO[CH_2N(NO_2)]_xCH_2OAc$ (x = 1-4).

Experimental

1,1,1,7,7,7-Hexanitro-3,5-dioxaheptane (2). 2,4,6-Trinitro-2,4,6-triazaheptane-1,7-diol diacetate (1.62 g, 4.6 mmol) was added with vigorous stirring to a suspension of 2,2,2-trinitroethanol (3.38 g, 18.7 mmol) in 13 mL of concentrated H_2SO_4 at 14 to 15 °C. In 10 min the temperature of the mixture increased to 20 to 22 °C. The mixture was kept at this temperature for 1 h and then poured onto crushed ice (100 g). The precipitate formed was filtered off, washed with water to a neutral reaction, and dried in air. After double recrystallization from CCl₄, white needles of product 2 were obtained (1.47–1.51 g, 86–88 % yield, m.p. 63–64 °C). Found (%): C, 16.2; H, 1.8; N, 22.5. C₅H₆N₆O₁₄. Calculated (%): C, 16.17; H, 1.61; N, 22.45. ¹H NMR (MeCN), δ : 4.97 (s, 2 H, CH₂); 5.06 (s, 4 H, CH₂).

1,1,1,5,5,5-Hexanitro-3-azapentane (3). **a.** 2,4,6-Trinitro-2,4,6-triazaheptane-1,7-diol diacetate (4 g, 11 mmol) was added to an emulsion of trinitromethane (6.4 g, 42 mmol) in 34 mL (638 mmol) of concentrated H₂SO₄ at 26-30 °C with vigorous stirring for 3-5 min, which was accompanied by strong frothing and heating to 35-40 °C. Then the reaction mixture was stirred for 60-80 min at 28-33 °C, cooled to ~20 °C, and poured onto crushed ice (250 g). In 15-20 min the precipitate was filtered off, washed with water to a neutral reaction, and dried in air. After recrystallization from CHCl₃, white needles of product 3 were obtained (1.1 g, 28.4 % yield, m.p. 107-108 °C, d₄²⁰ 1.83 g/cm³). Found (%): C, 13.8; H, 1.4; N, 28.9. C₄H₅N₇O₁₂. Calculated (%): C, 14.00; H, 1.47; N, 28.57. ¹H NMR (MeCN, SiMe₄), δ : 4.45 (d, 2 H, CH₂, ³J_{CH-NH} = 8.0 Hz); 3.3 (q, H, NH).

b. 2,4,6-Trinitro-2,4,6-triazaheptane-1,7-diol diacetate (8 g, 225 mmol) was added to concentrated H_2SO_4 (68 mL, 1276 mmol) over 5 min, which was accompanied by strong frothing. Then trinitromethane potassium salt (16 g, 85 mmol) was added over 5 min at a temperature not higher than 50–55 °C. The reaction mixture was stirred for 20–25 min at 40–45 °C, then cooled to ~20 °C, and poured on crushed ice. The precipitate formed was filtered off, washed with water to a neutral reaction, and dried in air. After recrystallization from CCl₄, product 3 (2.2 g, 28.4 % yield, m.p. 106–108 °C) was obtained. ¹H NMR (MeCN, SiMe₄), δ : 4.45 (d, 2H, CH₂, ³J_{CH-NH} = 8.0 Hz); 3.3 (q, H, NH).

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