Synthesis and crystal structure of 4-acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide

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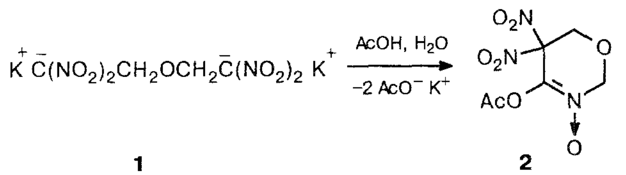
A novel heterocyclic compound, 4-acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide, has been synthesized by the reaction of the dipotassium salt of 1,1,5,5-tetranitro-3-oxapentane with aqueous acetic acid. The synthesized compound has been studied by X-ray diffraction analysis.

Key words: dipotassium salt of 1,1,5,5-tetranitro-3-oxapentane; 4-acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide; 2-cyano-2-nitroethanol; 2,2-dinitroethanol; acetic acid; intramolecular cyclization.

Previously[1] it was found that when the dipotassium salt of 1,1,5,5-tetranitro-3-oxapentane (**1**)[2] reacts with aqueous AcOH, a new type of intramolecular cyclization occurs to afford a hitherto unknown heterocyclic compound, 4-acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide (**2**) in a 59 % yield.



1 **2**

It is possible to perform intramolecular cyclization over a wide temperature range from 0 to 40 °C at a concentration of AcOH from 99 to 60 %; however, compound **2** is obtained in the maximum yield (59 %) in 80 % AcOH medium at 20 °C.

Increasing the reaction temperature causes the contamination of the product and a decrease in its yield due to decomposition of aliphatic dinitro compounds in an acidic medium. Decreasing the temperature to values lower than 0 °C sharply decreases the rate of the reaction. The termination of the reaction was detected visually from the disappearance of the yellow color of the reaction mixture and from the evolution of gas bubbles on the walls of the flask.

Experimental

NMR spectra were recorded on a spectrometer (300 MHz), produced at the Experimental Plant of Scientific Instruments, Russian Academy of Sciences (Chernogolovka). IR spectra were recorded on a Specord M-80 spectrophotometer.

4-Acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide (2). An 80 % solution of AcOH (200 mL) was placed into a three-neck flask equipped with a mechanical stirrer and a thermometer, and compound **1** (9 g, 0.0272 mol) was added at 19—22 °C with vigorous stirring; after stirring for 10 min, 400 mL of water was added. The white precipitate that formed was filtered off, dried in air, and recrystallized from $CHCl_3$. Colorless crystals of **2** (4.03 g, 59.3 %) were obtained, m.p. 100—101 °C. Found (%): C, 28.8; H, 2.9; N, 16.7. $C_6H_7N_3O_8$. Calculated (%): C, 28.92; H, 2.82; N, 16.87. NMR (CD_3CN, TMS, δ): 2.22 (s, 3 H, CH_3); 4.63 (br.s, 2 H, CH_2); 5.0 (br.s, 2 H, CH_2). On cooling, an AB-type spectrum appears: Δδ ~55 Hz (δ = 5.0); Δδ = 10 Hz (δ = 4.63).

IR (acetone, ν/cm^{-1}): 1760 (C=O); 1602, 1588, 1316 [$C(NO_2)_2$]; 1293 (N^+—O^-); 1115 (C—O—C).

The crystals of $C_6H_7N_3O_8$ (**2**), mol. weight 249.15, are orthorhombic, a = 23.413(8), b = 14.285(5), c = 5.900(6) Å; V = 1974(2) Å^3, d_{calc} = 1.676 g cm^{-3}, λ = 0.7107 Å; space group is *Pcab*, Z = 8; 620 independent reflections observed in the range $0.002 < \sin\theta/\lambda < 0.5$ Å^{-1} were collected on a four-circle KM-4 diffractometer (KUMA-Diffraction, Poland) using the ω/2θ-scanning technique (parallelepiped-shaped crystals, 0.4×0.3×0.2 mm).

The structure was solved by the direct method on a personal computer (SATO) using the SHELX-86 program package. Atomic coordinates (Table 1) were refined by the full-matrix least-squares method to R = 0.051; the temperature parameters were refined anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms. Coordinates of hydrogen atoms were determined directly from the electron density synthesis.

Results and Discussion

The compound studied is a six-membered heterocycle with three functional groups: *gem*-dinitromethyl, acetoxy, and *N*-oxide groups (Fig. 1). The cycle adopts

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Table 1. Atomic coordinates ($\times 10^4$) for the structure of **2**

Atom	x	y	z
O(1)	3422(2)	4502(7)	381(8)
O(2)	3957(2)	4480(6)	−2789(8)
O(3)	4762(3)	2934(6)	2441(9)
O(4)	2960(3)	3487(6)	3984(9)
O(5)	3026(2)	2021(7)	2952(9)
O(6)	4034(3)	1891(6)	−918(9)
O(7)	3293(3)	2723(6)	−1655(9)
N(1)	3185(3)	2840(7)	2991(8)
N(2)	3693(3)	2481(7)	−467(8)
N(3)	4325(3)	4480(7)	2010(8)
C(1)	3848(4)	3985(8)	1405(9)
C(2)	3759(3)	3043(8)	1793(9)
C(3)	4234(4)	2610(8)	3225(9)
C(4)	4823(4)	3904(8)	2935(9)
C(5)	3536(4)	4737(8)	−1899(9)
C(6)	3049(4)	5304(9)	−2727(9)
H(1)	3155(10)	5496(15)	−4177(25)
H(2)	3133(15)	5979(20)	−1581(30)
H(3)	2754(15)	5030(20)	−3288(35)
H(4)	5136(10)	4005(17)	1727(40)
H(5)	4994(15)	3986(17)	4574(35)
H(6)	4335(10)	1909(20)	3602(40)
H(7)	4130(15)	2855(20)	4974(35)

a flattened *twist* conformation: the C(2), C(1), N(3), C(4), O(8), and O(1) atoms are nearly in a plane, the C(3) and O(3) atoms lie above and below this plane. The atoms of the acetoxyl group lie in the plane that forms an angle of 76.4° to the planar fragment of the cycle; the angle between the planes of the nitro groups is 103°.

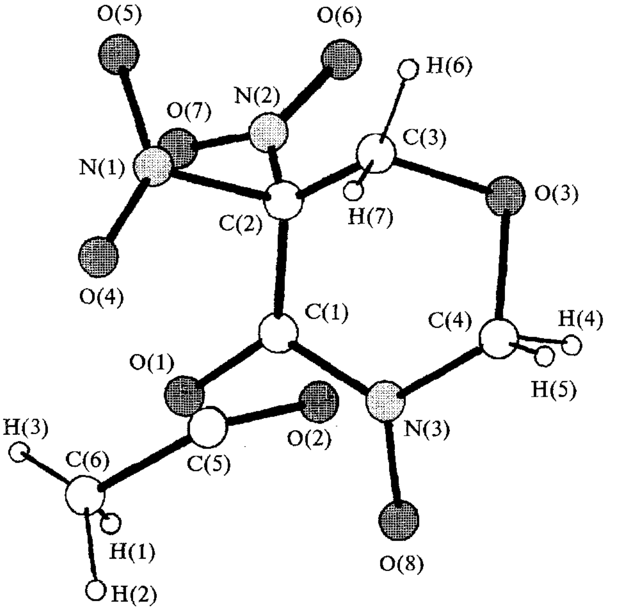


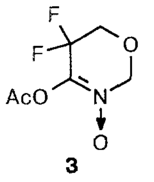
Fig. 1. Molecule of 4-acetoxy-5,6-dihydro-5,5-dinitro-2*H*-1,3-oxazine *N*-oxide.

The O(1)—O(8) bond length in the molecule (2.63 Å), may be considered as shortened because the O(1)C(1)N(3) bond angle (115.2(5)°) is smaller than the O(1)C(1)C(2) bond angle (119.4(5)°), while the C(1)N(3)O(8) and O(8)N(3)C(4) bond angles are 122.0(5)°.

This fact, along with the planar conformation of the O(1)C(1)N(3)O(8) fragment, which attests that the orbitals of the lone electron pairs of the O(1) and O(8) atoms have the same symmetry, suggests the interaction between these orbitals. The lone electron pairs of the O(1) and O(8) atoms are directed toward each other, and their interaction should cause the formation of a bonding MO with slight stabilization and an antibonding MO with substantial destabilization of the molecular level. The antibonding combination may interact with the σ*(C=N) MO. Interaction between levels occurs with the transfer of charge from the antibonding region, due to which the interaction between the lone electron pairs becomes attractive. In molecule **2**, this interaction is manifested in the bond lengths in the given fragment. Thus, the C=N double bond is substantially elongated, with a length of 1.373(8) Å compared to the commonly accepted double bond length of 1.27 Å, whereas the C(1)—O(1) and N(3)—O(8) bonds are shortened: the length of the former is 1.381(5) Å and is smaller than the corresponding values for the same ether bonds in the cycle (O(3)—C(3) (1.399(5) Å) and C(4)—O(3) (1.423(5) Å)). The N(3)—O(8) bond (1.229(5) Å) is substantially shorter than the analogous distances in alkoxydiazene *N*-oxides (1.26 Å).[3]

The criterion for the validity of these reasonings may be the populations between the interacting atomic centers. Because of limitations of the program, *ab initio* quantum-chemical calculations were performed for model molecule **3**, which has a smaller number of atoms.

Calculations for molecule **3** were performed using the MONSTERGAUSS-81 program with the minimum basis (STO-3G) and full geometry optimization. Calculations demonstrated that the four-atom —O—C=N→O fragment, whose conformation is identical to the conformation of the analogous fragment of molecule **2**, is a unified conjugated system with six π-electrons. The highest occupied MO φ_1 is π in character, weakens the O—C and N→O bonds and strengthens the C(1)—N(3) bond; the π system of the —O—C=N→O fragment is characterized by attraction between the terminal oxygen atoms. The φ_2 MO, which is σ in character, represents an analogous type of bonding (Fig. 2).



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The highest occupied MOs φ_1 and φ_2 make the greatest contribution to the positive value of the overlap population of the oxygen atoms: the atomic coefficients are large and positive. The attractive interaction between the oxygen atoms stabilizes the conformation of the complex overcrowded molecule of **2**.

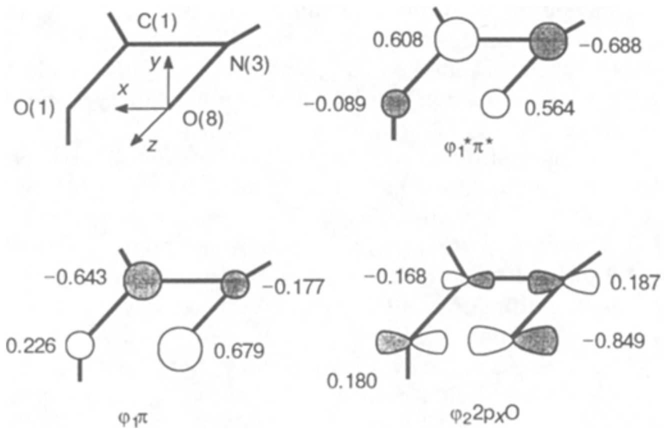
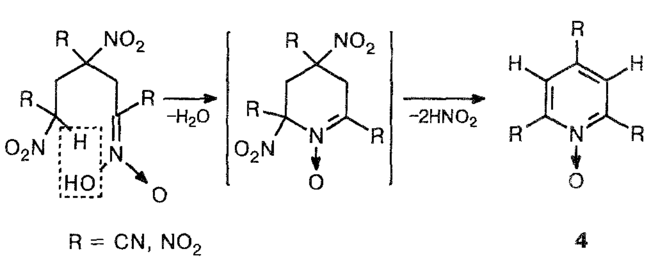


Fig. 2. Distribution of the highest occupied MOs and the lowest unoccupied MOs in the four-atom —O—C=N→O fragment.

It is of interest to elucidate the mechanism of the synthesis of *N*-oxide **2**. We found three papers concerning the synthesis of six-membered heterocyclic compounds with an *N*-oxide group from aliphatic compounds containing terminal *gem*-dinitromethyl groups.[4—6] The cyclization of aliphatic *gem*-dinitromethyl compounds was first reported back in the beginning of this century.[4] The authors obtained a product with the empirical formula $C_5H_2N_4O_7$ and m.p. 186 °C in a 30 % yield by the reaction of the potassium salt of 2,2-dinitroethanol with dilute aqueous sulfuric acid. At that time, the structure of the synthesized product was not established. More recently, the synthesis of 2,4,6-tricyanopyridine *N*-oxide by the reaction of dilute sulfuric acid with the potassium salt of 2-cyano-2-nitroethanol (the yield is 50 %) was reported.[5] These authors suggested[5] that 2,4,6-trinitropyridine *N*-oxide had been obtained previously.[4] Finally, the structure of 2,4,6-trinitropyridine *N*-oxide, obtained when 2,2-dinitroethanol was heated at 50—60 °C in water (the yield is 10 %) or when 1,1,3,3,5,5-hexanitropentane was stored in aqueous ethanol (the yield is 75 %), was established unambiguously.[6] An examination of the chemical properties of samples of 2,4,6-trinitropyridine *N*-oxide prepared by different methods[4,6] demonstrated that they were completely identical. It was suggested[6] that in the case of 2-cyano-2-nitro- and 2,2-dinitroethanols, 1,3,5-trinitro-substituted pentanes are formed by the reaction of double dinitroethylation, first of the initial nitroalcohols and then of the Michael adducts. The intramolecular cyclization of 1,3,5-trinitro-substituted pentanes with the elimination of a water molecule affords symmetrically substituted *N*-oxides, which are stabilized to form a pyridinium system through the elimination of two molecules of nitrous acid (Scheme 1).

Scheme 1



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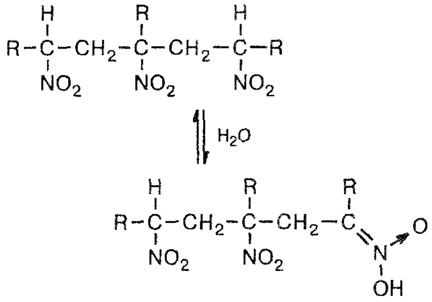
In the framefowk of this tentative mechanism, some features of the cyclization of 1,3,5-trinitro-substituted pentanes into six-membered heterocycles with *N*-oxide groups should be specified. Characteristically, the formation of symmetrically substituted pyridine *N*-oxides occurs without the cleavage of the carbon—carbon bonds in the initial polynitropentane. Another substantial point is the cyclization of *N*-oxide in the presence of water. It is the presence of water that favors the ionization of one of the terminal nitromethyl groups in polynitropentane to produce the reactive aci-form.



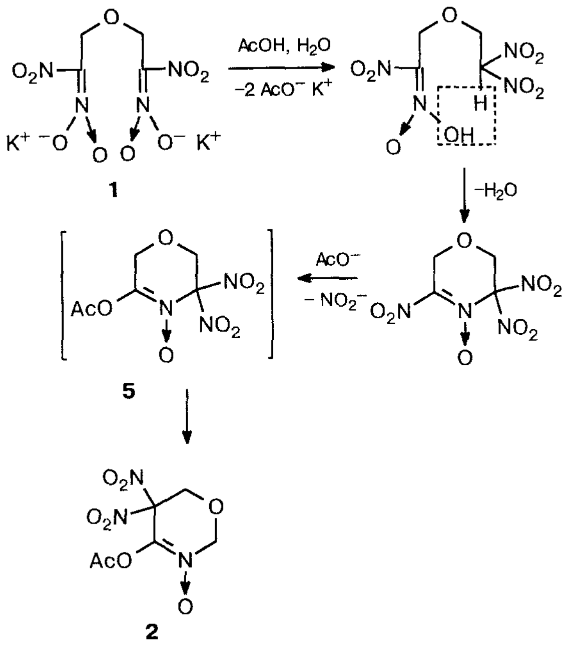
$$\mathrm{R{-}\underset{NO_2}{\overset{H}{C}}{-}CH_2{-}\underset{NO_2}{\overset{R}{C}}{-}CH_2{-}\underset{NO_2}{\overset{H}{C}}{-}R} \;\overset{H_2O}{\rightleftharpoons}\; \mathrm{R{-}\underset{NO_2}{\overset{H}{C}}{-}CH_2{-}\underset{NO_2}{\overset{R}{C}}{-}CH_2{-}\overset{R}{C}{=}\underset{OH}{N}{\rightarrow}O}$$

The removal of water causes the termination of the conversion of 2-cyano-2-nitro- and 2,2-dinitroethanols at the stage of the formation of 1,3,5-substituted nitropentane and isolation of the latter from the reaction in the nitro form as was shown[6] for the example of 1,1,3,3,5,5-hexanitropentane. And, of course, for this process to occur the initial substrate must be soluble in the reaction medium (water or aqueous ethanol) and the cyclic product formed must be insoluble.

Returning to the compound under consideration, the synthesis of **2** from 1,1,5,5-tetranitro-3-oxapentane can be shown by the following scheme (Scheme 2).

A common indicator of *N*-oxide cyclization of polynitro compounds both in known cases and in our case is the formation of the aci-form of one of the terminal dinitromethyl groups in substituted aliphatic polynitropentanes in a weakly acidic medium (aqueous H_2SO_4 or aqueous AcOH). This apparently results in the formation of a six-membered cycle containing the *N*-oxide fragment. The cyclic *N*-oxide is stabilized in a weakly acidic medium[6] through the elimination of elements of nitrous acid, which results in the synthesis of the stable substituted pyridine *N*-oxide cycle. In our

Scheme 2



case, stabilization occurs through the rearrangement of the cycle, which takes place during the nucleophilic substitution of an acetate ion for the nitro group adjacent to the *N*-oxide fragment.

The nitro group that is replaced is attached to a carbon atom involved in a partially aromatic multiple bond. This substitution proceeds as substitution with transfer.[7] Apparently, one must allow for the short-term existence of intermediates, one of which is the mixed anhydride of the *N*-oxide of cyanic and acetic acids, and the other of which is either the 3,3-dinitrooxetane or $H_2C^+—O—CH_2—C^-(NO_2)_2$ zwitter-ion. Note that we failed to perform *N*-oxide cyclization in the required direction when acetic acid was replaced with sulfuric, formic, and propionic acids even though we varied the reaction conditions over a wide range. Evidently, the rearrangement is possible only with the use of acetate ions. It may be suggested that the interaction between *N*-oxide and acetate groups that we observed in the crystal exists also in solution and is, therefore, the initial stage of cycle formation. In our case, unlike cyclization into substituted pyridine *N*-oxide,[6] the rearrangement of the cyclic six-membered *N*-oxide occurs with the cleavage of the carbon—carbon and carbon—nitrogen bonds in the cycle.

Quantum-chemical calculations with full geometry optimization for molecules **5** and **2** by the AM1 SCF MO LCAO method using hydrogen atoms instead of acetyl groups (which is a conventional approximation[8]) indicated a thermodynamic preference for structure **2**, with a difference in the calculated heats of formation of ~4.3 kcal mol^{-1}.

Therefore, the synthesis of the cyclic *N*-oxide **2** from dipotassium salt **1** performed in this work, as well as the preparation of 2,4,6-tricyano- and 2,4,6-trinitropyridine *N*-oxides, are examples of *N*-oxide cyclization in a series of aliphatic polynitropentanes with ionizable terminal nitromethyl groups.

The features revealed suggest the possibility of involving other polynitropentanes containing *gem*-dinitromethyl groups in *N*-oxide cyclization.

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