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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 75th anniversary

Nitro Derivatives of 1,3-Dihydrobenzimidazol-2-one: I. Synthesis of *N*-Nitrobenzimidazol-2-ones

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Abstract—1,3,5,6-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one, 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one, and 1,4,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one were synthesized for the first time by nitration of 5,6-di- and 4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-ones with concentrated nitric acid in acetic anhydride.

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Up to now, all C-nitro derivatives of 2,3-dihydro-1*H*-benzimidazol-2-one (**I**) that can be obtained by its direct nitration have been reported, and facile introduction of nitro groups into the benzene ring of **I** has been noted [1–5]. 5-Nitro derivative **II** is formed upon treatment of benzimidazolone **I** with 30% nitric acid [3], as well as in the nitration of **I** with an equimolar amount of 98% HNO_3 in sulfuric acid at 0°C [1]. 5,6-Dinitro derivative **III** was synthesized by heating compound **I** for a short time in 60–65% HNO_3 taken in large excess [2] or by reaction of **I** with an equimolar amount of 98% nitric acid in concentrated sulfuric acid at 5–10°C [1].

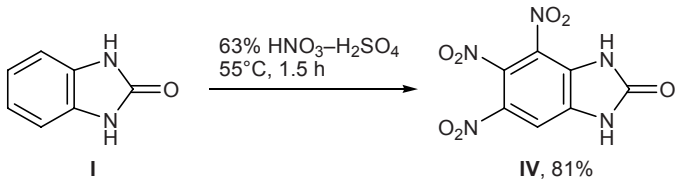
According to the data of [1, 2], 4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**IV**) can be obtained from compound **I** by heating in a large excess of 98% HNO_3 for a short time [2] or by nitration of **I** in sulfuric acid with an equimolar amount of 98% HNO_3 at 40–45°C [1]. Compound **IV** was purified from an impurity of **III** by recrystallization from ethanol [1] or water [2]. However, this procedure is inconvenient because of poor solubility of 4,5,6-trinitro derivative **IV** in the above solvents.

It was proposed to synthesize 4,5,6,7-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**V**) in two steps [1], the first of which was nitration of benzimidazolone **I** in sulfuric acid at 40–45°C until a mixture of compounds **II** and **III** was formed. The product mixture thus formed was nitrated in sulfuric acid at 100°C using a large excess of 98% HNO_3. The nitration of **I** with 98% HNO_3 in a mixture of acetic acid and acetic anhydride at 70°C also gave tetranitro derivative **V** [2].

Due to ready introduction of nitro groups into the benzene ring of compound **I** the synthesis of nitro derivatives **IV** and **V** requires no large excess of nitric acid. In addition, 4,5,6,7-tetranitrobenzimidazolone **V** is considerably better soluble in several solvents, as compared to 5,6-di- and 4,5,6-trinitro derivatives **III** and **IV**. Therefore, partial overnitration of the initial compound is advisable to ensure complete conversion of **III** (which is poorly soluble in organic solvents) and higher purity of product **IV**.

We performed nitration of benzimidazolone **I** to 4,5,6-trinitro derivative **IV** in sulfuric acid with the use of 50% excess of 63% HNO_3. The reaction at 55°C (1.5 h) gave compound **IV** containing no more than

Scheme 1.

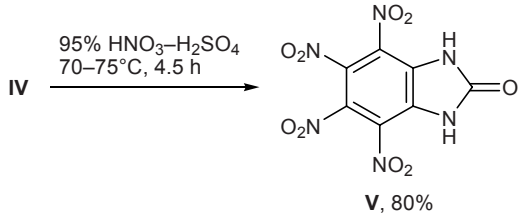


I **IV**, 81%

5 mol % of 4,5,6,7-tetranitrobenzimidazolone **V** (Scheme 1). The latter was removed from the crude product by treatment at 35–40°C with 40% aqueous ethanol where 4,5,6,7-tetranitro derivative **V** is soluble much better than in water or pure ethanol. Compound **IV** without additional purification can be brought into further nitration to obtain 4,5,6,7-tetranitrobenzimidazolone **V**.

4,5,6-Trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**IV**) was converted into 4,5,6,7-tetranitro derivative **V** by treatment at 70–75°C with 100% excess of 95% HNO_3 in sulfuric acid, the H_2SO_4–**IV** weight ratio being 9:1 (Scheme 2). 4,5,6-Trinitro derivative **IV** was consumed almost completely in 4.5 h, and 4,5,6,7-tetranitrobenzimidazolone **V** separated from the reaction solution. After cooling, filtration, and washing, the crude product contained no more than 0.3 mol % of compound **IV** (according to the HPLC data). The waste acid mixture may be reused after strengthening with oleum. 4,5,6,7-Tetranitrobenzimidazolone **V** may be additionally purified by recrystallization from 93–96% sulfuric acid or acetic acid.

Scheme 2.



V, 80%

Unlike C-nitro-substituted benzimidazol-2-ones, N-nitro derivatives of compound **I** were not reported previously. With a view to synthesize N,C-nitrobenzimidazolones we examined nitration of compounds **II**–**V** with nitric acid in acetic anhydride at relatively low temperature.

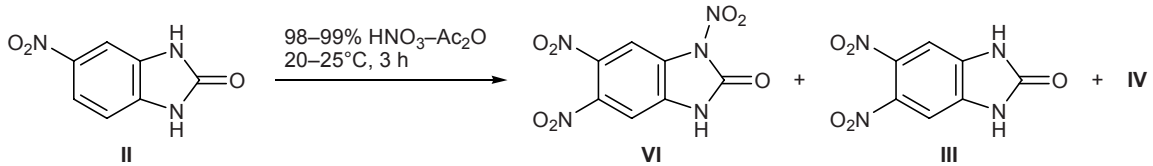
The nitration of **II** with excess nitric acid in acetic anhydride (HNO_3–Ac_2O molar ratio 2:1) at room temperature gave a mixture of 1,5,6-trinitro-, 5,6-dinitro-, and 4,5,6-trinitrobenzimidazolones **VI**, **III**, and **IV** at a weight ratio of 2:1:1 (Scheme 3). Compound **VI** separated from the reaction mixture as colorless crystals. After filtration, compounds **III** and **IV** were isolated by dilution of the filtrate with water. Separation of **III** from **IV** involved no difficulties due to poor solubility of 5,6-dinitro derivative **III** in organic solvents (in contrast to **IV**). The product ratio changed, depending on the composition of the acid mixture and amount of nitric acid. When the ratio of HNO_3 to acetic anhydride was reduced to equimolar, the yield of trinitrobenzimidazolones **IV** and **VI** decreased, and compound **III** became the major product. Our attempts to synthesize 1,5-dinitro- and/or 1,6-dinitro derivatives **VII** and **VIII** via further reducing the amount of nitric acid and temperature (to –10°C) were unsuccessful. Either compound **VI** was formed, or 5,6-dinitrobenzimidazolone **III** was isolated as the only product.

Our further experiments on nitration of 5-nitrobenzimidazolone **II** with excess concentrated nitric acid in acetic anhydride (molar ratio 2:1) showed that the composition of nitration products strongly depends on the reaction temperature. When 5-nitrobenzimidazolone **II** was added to the nitrating mixture at 15–20°C, N-mononitro derivative **VI** (1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one) separated. Raising the temperature to 35°C resulted in the formation of *N*,*N*′-dinitro derivative, 1,3,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**IX**) in 47% yield (Scheme 4). After separation of compound **IX** by filtration, the filtrate was poured onto ice. We thus obtained a mixture of nitration products, which contained (according to the HPLC and ^{1}H NMR data) 1,3,5,6-tetranitro-, 1,5,6-trinitro-, and 1,4,5,6-tetranitro derivatives **IX**, **VI**, and **X** at a molar ratio of 1:2.5:8.5.

N-Nitro derivative **VI** can be synthesized in 56% yield by nitration of benzimidazolone **I** with an equimolar mixture of nitric acid and acetic anhydride (6 equiv of HNO_3).

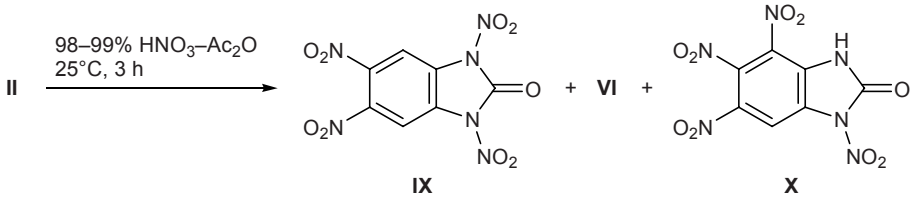
Nitration of 5,6-dinitrobenzimidazolone **III** also led to different products. The reaction of **III** with an equimolar mixture of nitric acid and acetic anhydride at room temperature gave mono-*N*-nitro derivative, 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**VI**), while the nitration with a 2:1 HNO_3–Ac_2O mixture resulted in the formation of a mixture of com-

Scheme 3.



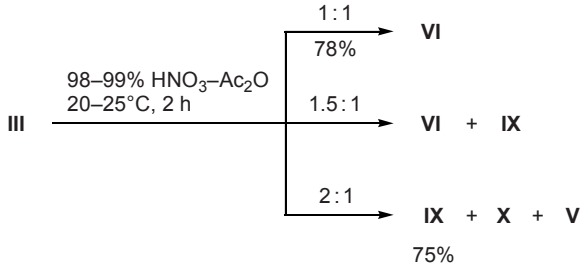
II **VI** **III**

Scheme 4.

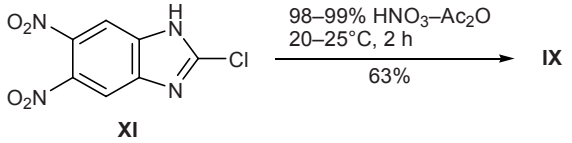


pounds **IX**, **X**, and **V** (Scheme 5). Compound **IX** separated from the reaction mixture as colorless crystals, and was isolated by filtration, and the filtrate was evaporated under reduced pressure and analyzed. As might be expected, a mixture of N-nitro compounds **VI** and **IX** was obtained when the amount of nitric acid was reduced to an HNO_3–Ac_2O molar ratio of 1.5:1, other conditions being equal. Compound **IX** was also synthesized by nitration of 2-chloro-5,6-dinitro-1*H*-benzimidazole (**XI**) under analogous conditions (Scheme 6).

Scheme 5.

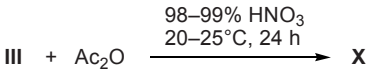


Scheme 6.



As expected, the product composition in the nitration of 5,6-dinitrobenzimidazolone **III** with excess concentrated nitric acid in acetic anhydride (molar ratio 2:1) strongly depended on the order of mixing of the reactants. Addition of compound **III** to a preliminarily prepared mixture of nitric acid and acetic anhydride at room temperature resulted in the formation of *N*,*N*′-dinitro derivative **IX**. When HNO_3 was added under analogous conditions to a suspension of **III** in acetic anhydride, 1,4,5,6-tetranitrobenzimidazolone **X** was obtained as the major product (yield 62%, Scheme 7) with an impurity of ~10 mol % of 4,5,6,7-tetranitrobenzimidazolone **V** (according to the HPLC data).

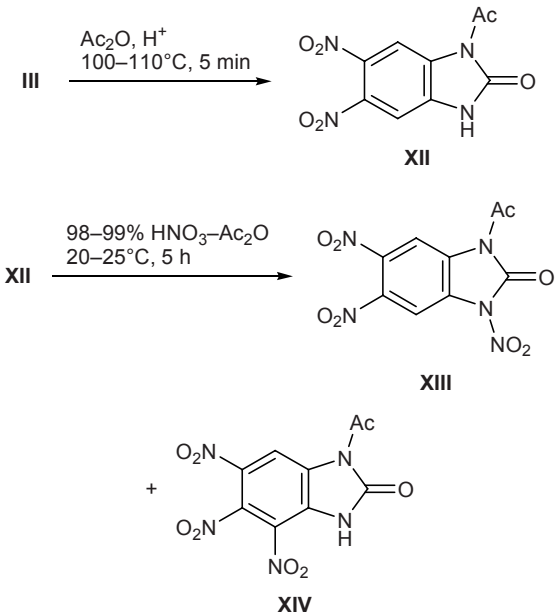
Scheme 7.



Taking into account that the formation of acetyl nitrate and nitrogen(V) oxide necessary for nitration at the nitrogen atom requires some time [6], the above findings suggest that compound **III** is partially protonated at the benzene ring with subsequent N-nitration. On the other hand, increased acidity of the reaction mixture in the initial step (due to the presence of free HNO_3) is likely to promote sharp acceleration of the acid-catalyzed N→C transfer of the nitro group to the benzene ring (like Bamberger rearrangement [7, 8]).

Unlike 5,6-dinitrobenzimidazolone **III**, 1-acetyl-5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XII**) undergoes nitration with excess nitric acid in acetic anhydride at room temperature at both nitrogen and aromatic carbon atoms. From the reaction mixture we isolated a mixture of 1-acetyl-3,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XIII**) and 1-acetyl-4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XIV**) at

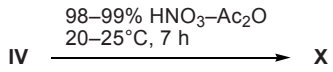
Scheme 8.



a molar ratio of 1:2 (Scheme 8). Trinitro derivative **XIV** was also synthesized independently, by acylation of 4,5,6-trinitrobenzimidazolone **IV** with acetic anhydride on heating in the presence of sulfuric acid.

N-Nitration of 4,5,6-trinitrobenzimidazolone **IV** with a mixture of nitric acid and acetic anhydride occurs at a considerably lower rate as compared to the nitration of **III**. As in the reactions with 5-mono- and 5,6-dinitro derivatives **II** and **III**, the product gradually separated as colorless crystals from the reaction mixture; however, much longer time is necessary to achieve an acceptable yield. The nitration with HNO_3–Ac_2O (molar ratio 2:1) gave 43% of compound **X** in 7 h (Scheme 9).

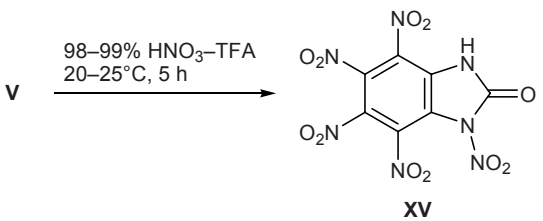
Scheme 9.



With the use of an equimolar mixture of nitric acid and acetic anhydride, other conditions being equal, *N*-nitro derivative **X** was obtained only in 34% yield. N-Nitration of 4,5,6-trinitrobenzimidazolone **IV** with a mixture of nitric acid and trifluoroacetic anhydride occurred at a considerably higher rate and with higher conversion. The reaction at room temperature gave 68% of compound **X** in 1 h. The process looks similar to the nitration in acetic anhydride. The reaction mixture gradually becomes homogeneous, and colorless crystals of 1,4,5,6-tetranitro derivative **X** begin to separate from the solution after a short time.

Our attempts to effect nitration of 4,5,6,7-tetranitrobenzimidazolone **V** in Ac_2O were unsuccessful, but the reaction in trifluoroacetic anhydride was similar to the nitration of 4,5,6-trinitro derivative **IV**. Initial yellow 4,5,6,7-tetranitrobenzimidazolone **V** dissolved to give a colorless solution, and colorless crystalline product separated in a short time (Scheme 10). After filtration and washing with trifluoroacetic acid on a filter on exposure to air, we observed vigorous decomposition of the product with liberation of nitrogen oxide and formation of yellow crystals of initial

Scheme 10.



XV

4,5,6,7-tetranitrobenzimidazolone **V**. Compound **XV** is unstable to the action of water and organic solvents, as well as of anhydrous carboxylic acids and their anhydrides, except for trifluoroacetic anhydride; therefore, we failed to obtain its satisfactory ^1H and ^{15}N NMR spectra. Taking into account the above stated, we presumed that the colorless crystalline product is N-nitro derivative, most probably 1,4,5,6,7-pentanitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XV**).

The newly synthesized N-nitro-substituted benzimidazolones **VI**, **IX**, and **X** are crystalline substances with low decomposition points, and they are unstable in solution. After removal of traces of strong acids by vacuum drying over alkali, crystalline compounds **VI**, **IX**, and **X** can be stored in a closed vessel for at least several months without appreciable decomposition. The structure of compounds **VI**, **IX**, and **X** was confirmed by the ^1H NMR and IR spectra and elemental analyses (see Experimental).

EXPERIMENTAL

The IR spectra were recorded from samples prepared as KBr pellets on a Shimadzu FTIR 8400 spectrometer. The ^1H NMR spectra were measured on a Bruker WM-400 instrument at 400 MHz using hexamethyldisiloxane as internal reference. The elemental compositions were determined on a Hewlett–Packard 185B CHN analyzer. The products were analyzed by HPLC on a Milikhrom liquid chromatograph equipped with a UV detector (λ 250 nm) and data acquisition and processing system. Product mixtures were separated in a Silasorb C_{18} column, 63 × 2 mm (grain size 5 μm, Lachema, Czechia); eluent water–acetonitrile–acetic acid (100:22:1, by weight), flow rate 100 μl × min^{-1}; sample volume 2–4 μl. The retention times were as follows (in order of elution): **III**, 243 s; **IV**, 380 s; **X**, 485 s; I**X**, 569 s; **V**, 957 s. The components were quantitated by the internal normalization technique using calibration coefficients.

Initial compounds **II**, **III**, and **XI** were synthesized according to the procedures described in [2, 9].

4,5,6-Trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (IV). Compound **I**, 41 g (0.306 mol), was dissolved in 360 ml of 93% H_2SO_4, and 140 g (1.400 mol) of 63% nitric acid was added at such a rate that the temperature of the mixture did not exceed 55°C. The mixture was kept for 1.5 h at 55°C, cooled to room temperature, poured into 1.5 l of cold water, and stirred for 30 min. The precipitate was filtered off and washed

with water. According to the HPLC data, the product contained 3–4 mol % of compound **V**. To remove the latter, the crude product was dispersed in 250 ml of 40% aqueous ethanol, thoroughly stirred for 15 min at 35°C, and the precipitate was filtered off and washed with ethanol. After purification, the concentration of **V** in the product was 0.4 mol %. Yield 66.7 g (81%), light yellow crystals, mp 313–315°C (decomp.); published data [2]: mp 313–314°C. IR spectrum, ν, cm^{-1}: 3145 (C–N, CH), 1752 (CH), 1644 (C=O), 1615 (C=O, C=C), 1550 ($ArNO_2$), 1492 (C=C), 1452, 1424, 1360 (C=C), 1330 ($ArNO_2$), 1267 (N–NO_2), 1196 (C–N), 976 (N–N), 919, 886, 835 (CH), 778 (CH), 751 (N–NO_2), 745 (N–NO_2), 676, 654, 623. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.65 s (1H, NH), 12.25 s (1H, NH), 7.95 s (1H, CH_{arom}). Found, %: C 31.30; H 1.24; N 25.93. $C_7H_3N_5O_7$. Calculated, %: C 31.24; H 1.12; N 26.02.

4,5,6,7-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (V). Compound **IV**, 10 g (37.2 mmol), was mixed at room temperature with 50 ml of 93% H_2SO_4, 6 g (90.5 mmol) of 95% HNO_3 was added, and the mixture was stirred for 4.5 h at 70–75°C. The mixture was cooled to 20°C, and the precipitate was filtered off and dispersed in 150 ml of water, the suspension was thoroughly stirred, and the precipitate was filtered off, washed with water, and dried at 80°C. Yield 9.5 g (80%), bright yellow crystals, mp 317–319°C (decomp.); published data [2]: mp 317°C. IR spectrum, ν, cm^{-1}: 3401 (NH), 3138, 1752 (C_{arom}), 1618 (C=O, C=C), 1550 (NO_2), 1501 (C=C), 1400 (C=C), 1339 (NO_2), 1206 (N–NO_2), 1054, 987, 931, 911, 864 (C_{arom}), 760, 690, 443. ^{1}H NMR spectrum (DMSO-d_6): δ 13.0 ppm, br.s (2H, NH). Found, %: C 26.76; H 0.69; N 26.63. $C_7H_2N_6O_9$. Calculated, %: C 26.77; H 0.64; N 26.75.

1,5,6-Trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (VI). *a*. Nitric acid (98–99%), 6 g (93.3 mmol), was added at 20–25°C to 10 g (98 mmol) of acetic anhydride, and 2 g (14.9 mmol) of compound **I** was added in portions at such a rate that the temperature of the mixture did not exceed 25°C. The mixture was stirred for 3 h at 25°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. Yield 2 g (50%), colorless crystals, mp 140–142°C (decomp.). IR spectrum, ν, cm^{-1}: 3362 (NH), 3164 (C–H), 3133 (C–H), 3078 (C–H), 1773 (CH), 1629 (C=O), 1593 (C=O, C=C), 1546 (NO_2), 1487 (C=C), 1460 (C=C), 1404, 1365, 1339 (NO_2), 1253 (N–NO_2), 1229, 1170 (NH), 1129, 1079 (N–N), 981, 892, 856, 826 (CH), 743 (CH), 719 (N–NO_2), 654, 619, 560 (N–NO_2). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.90 s (1H, H_{arom}), 8.55 s (1H, H_{arom}), 12.05 s (1H, NH). Found, %: C 31.34; H 1.56; N 25.94. $C_7H_3N_5O_7$. Calculated, %: C 31.24; H 1.12; N 26.02.

b. Nitric acid (98–99%), 3.5 ml, was added at 20–25°C to 8 ml of acetic anhydride, and 2 g (8.9 mmol) of compound **III** was added in small portions at such a rate that the temperature did not exceed 20°C. The mixture was stirred for 2 h at 20°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. Yield 1.9 g (78%), colorless crystals, mp 141–143°C (decomp.).

1,3,5,6-Tetranitrobenzimidazol-2-one (IX). Nitric acid (98–99%), 7 ml, was added at 20–25°C to 8 ml of acetic anhydride, and 1 g (4.1 mmol) of 2-chloro-5,6-dinitro-1*H*-benzimidazole (**XI**) was added in portions at such a rate that the temperature did not exceed 25°C. The mixture was stirred for 2 h at 25°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. Yield 0.82 g (63%), colorless crystals, mp 120–122°C (decomp.). IR spectrum, ν, cm^{-1}: 3390, 3135 (CH), 2887 (CH), 1818 (CH), 1633 (C=O), 1606 (C=O, C=C), 1543 (NO_2), 1470 (C=C), 1385 (C=C), 1361 (NO_2), 1267 (N–NO_2), 1232, 1140 (NH), 1060 (N–N), 910, 890, 853, 820 (CH), 770 (CH), 757 (N–NO_2), 733, 703 (N–NO_2), 657. ^{1}H NMR spectrum (acetone-d_6): δ 8.80 ppm, s (H_{arom}). Found, %: C 26.77; H 0.64; N 26.75. $C_7H_2N_6O_9$. Calculated, %: C 26.50; H 0.61; N 26.54.

1,4,5,6-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (X). *a*. Acetic anhydride, 8 ml, was mixed at 20–25°C with 7 ml of 98–99% HNO_3, and 1 g (3.7 mmol) of compound **IV** was added in small portions. The mixture was stirred for 7 h at 20°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. Yield 0.44 g (43%), colorless crystals, mp 144–145°C (decomp.). IR spectrum, ν, cm^{-1}: 3435 (NH), 3126 (C–N, CH), 1825, 1796 (CH), 1622 (C=O, C=C), 1558 (NO_2), 1484 (C=C), 1446, 1398 (C=C), 1345 (NO_2), 1259 (N–NO_2), 1152 (C–N), 1082, 931 (N–N), 822 (CH), 760 (CH), 740 (N-NO_2), 664, 649, 564. ^{1}H NMR spectrum (acetone-d_6): δ 8.95 ppm, s (1H, H_{arom}). Found, %: C 26.89; H 0.79; N 26.83. $C_7H_2N_6O_9$. Calculated, %: C 26.77; H 0.64; N 26.75.

b. Trifluoroacetic anhydride, 24 ml, was mixed at 5–10°C with 7 ml of 98–99% HNO_3, 1 g (3.7 mmol) of

compound **IV** was added, and the mixture was stirred for 1 h at 20°C. The precipitate was filtered off, washed with a small amount of trifluoroacetic acid, and dried in air at room temperature. Yield 0.8 g (69%), colorless crystals, mp 144–145°C (decomp.).

Nitration of 5-nitro-2,3-dihydro-1*H*-benzimidazol-2-one (II) with nitric acid in acetic anhydride. *a*. Nitric acid (98–99%), 7 ml, was added at 20–25°C to 8 ml of acetic anhydride, and 2 g (11.1 mmol) of compound **II** was added in small portions at such a rate that the temperature did not exceed 20°C. The mixture was stirred for 3 h at 20°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over sodium hydroxide. The product was 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**VI**), yield 1 g (33%), colorless crystals, mp 141–142°C (decomp.).

The filtrate was poured onto ice, the mixture was left overnight, and the precipitate was filtered off, washed with water, and dried in air. The product, 1 g, was a mixture consisting of 5,6-di- and 4,5,6-trinitro derivatives **III** and **IV** at a molar ratio of 1:1. It was thoroughly stirred with acetone at room temperature, and the precipitate was filtered off and washed with acetone to obtain 0.45 g (18%) of 5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**III**). The acetone filtrate was evaporated to isolate 0.47 g (16%) of 4,5,6-trinitrobenzimidazolone **IV**.

b. Nitric acid (98–99%), 14 ml, was added at 20–25°C to 16 ml of acetic anhydride, and 4 g (22.2 mmol) of compound **II** was added in small portions at such a rate that the temperature did not exceed 35°C. The mixture was kept for 3 h at 25°C, and the precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. We thus isolated 3.3 g (47%) of 1,3,5,6-tetranitrobenzimidazolone **IX** as colorless crystals with mp 120–122°C (decomp.).

The filtrate was poured onto ice. After 30 min, the precipitate was filtered off, washed with water, and dried in air. The product was 1.71 g of a mixture consisting of 1,3,5,6-tetra-, 1,5,6-tri-, and 1,4,5,6-tetranitro derivatives **IX**, **VI**, and **X** at a molar ratio of 1:2.5:8.5 (according to the ^{1}H NMR and HPLC data).

Nitration of 5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (III) with nitric acid in acetic anhydride (molar ratio 2:1). *a*. Acetic anhydride, 50 ml, was mixed at 20–25°C with 50 ml of 98–99% HNO_3, 7 g (31.2 mmol) of compound **III** was added in small portions, and the mixture was stirred for 2 h at 20°C. The precipitate was filtered off, thoroughly washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. Yield of 1,3,5,6-tetranitrobenzimidazolone **IX** 6.6 g (67%), colorless crystals, mp 120–121°C (decomp.).

The filtrate was poured onto ice, the mixture was kept for 30 min, and the precipitate was filtered off, washed with water, and dried in air. The product was 1.75 g of a mixture consisting of 1,4,5,6- and 4,5,6,7-tetranitro derivatives **X** and **V** at a weight ratio of 2.3:1 (according to the ^{1}H NMR and HPLC data).

b. Compound **III**, 7 g (31.2 mmol), was dispersed at room temperature in 50 ml of acetic anhydride, and 50 ml of 98–99% HNO_3 was slowly added to the suspension, maintaining the temperature at 15–20°C. The mixture was stirred for 24 h at 20°C and poured onto ice (~500 ml of water); after 30 min, the precipitate was filtered off, washed with water, and dried in air. The product was 7.0 g (62%) of 1,4,5,6-tetranitrobenzimidazolone **X** colored yellow due to the presence of 4,5,6,7-tetranitrobenzimidazolone **V** as an impurity (~10 mol %, according to the HPLC data).

1-Acetyl-5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (XII). Compound **III**, 5 g (22.3 mmol), and 93% H_2SO_4, 1–2 drops, were added at room temperature to 10 ml of acetic anhydride. The mixture was heated for 5 min at 100–110°C and cooled to room temperature, and the precipitate was filtered off, thoroughly squeezed, washed with acetic anhydride and diethyl ether, and dried in air. Yield 4.2 g (71%), light brown crystals, mp 234–236°C (decomp.; from ethanol). IR spectrum, ν, cm^{-1}: 3462, 3130 (C–N), 3026 (CH), 1741 (CH), 1628 (C=O), 1609 (C=O, C=C), 1545 (NO_2), 1486 (C=C), 1410, 1358 (C=C), 1340 (NO_2), 1297 (N–NO_2), 1238 (C–N), 1158, 1105, 1053 (N–N), 1038, 997, 896, 880, 847 (CH), 834 (CH), 750 (N–NO_2), 707 (N–NO_2), 686, 626. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.48 s (1H, NH), 8.60 s (1H, H_{arom}), 7.70 s (1H, H_{arom}), 2.70 s (3H, CH_3). Found, %: C 40.76; H 2.58; N 21.44. $C_9H_6N_4O_6$. Calculated, %: C 40.61; H 2.27; N 21.05.

1-Acetyl-4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (XIV). Compound **IV**, 2 g (7.4 mmol), and 93% H_2SO_4, 1–2 drops, were added at room temperature to 5 ml of acetic anhydride, the mixture was heated for 5 min at 100–110°C and cooled to room temperature, and the precipitate was filtered off, thoroughly squeezed, washed with acetic anhydride and diethyl ether and dried in air. Yield 1.80 g (78%), light yellow crystals, mp 252–254°C (decomp.; from etha-

nol). IR spectrum, ν, cm^{-1}: 3436 (NH), 3138 (C–N, CH), 1761 (CH), 1731 (C=O), 1623 (C=O), 1610 (C=O, C=C), 1570, 1558 (NO_2), 1550 (C–N, NH), 1488 (C=C), 1353 (C=C), 1334 (NO_2), 1315, 1279 (N–NO_2), 1185 (C–N), 1151, 1103, 1070 (N–N), 964, 917, 769 (CH, N–NO_2), 676 (N–NO_2), 654, 622. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.97 s (1H, H_{arom}), 2.70 s (3H, CH_3). Found, %: C 34.83; H 1.88; N 22.41. $C_9H_5N_5O_8$. Calculated, %: C 34.74; H 1.62; N 22.51.

1-Acetyl-3,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (XIII). Acetic anhydride, 8 ml, was mixed at 20–25°C with 7 ml of 98-99% HNO_3, and 1 g (3.7 mmol) of compound **XII** was added in small portions. The mixture was stirred for 5 h at 20°C, and the precipitate was filtered off, washed with 1,2-dichloroethane, and dried under reduced pressure over NaOH. The product, 0.2 g, was a mixture of 1-acetyl-3,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XIII**) and 1-acetyl-4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XIV**) at a molar ratio of 1:2 (according to the ^{1}H NMR and HPLC data).

The filtrate was poured into 75 ml of cold water; after 15 min, the precipitate was filtered off, washed with water, and dried in air. Yield 0.42 g (36%), mp 219–223°C (decomp.). IR spectrum, ν, cm^{-1}: 3421, 3133 (C–N, CH), 1806 (CH), 1630 (C=O), 1604 (C=O, C=C), 1545 (NO_2), 1476 (C=C), 1385 (C=C), 1319 (NO_2), 1263 (N–NO_2), 1229 (C–N), 1163, 1110, 1062 (N–N), 961, 892, 843 (CH), 785 (CH), 756 (N–NO_2), 732, 708 (N–NO_2), 623, 609. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 8.95 s (1H, H_{arom}), 8.68 s (1H, H_{arom}), 2.80 s (3H, CH_3). Found, %: C 34.46; H 1.72; N 22.83. $C_9H_5N_5O_8$. Calculated, %: C 34.74; H 1.62; N 22.51.

Nitration of 4,5,6,7-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (V) with nitric acid in trifluoroacetic anhydride. Trifluoroacetic anhydride, 25 ml, was mixed at 5–10°C with 7 ml of 98–99% HNO_3, 1 g (3.2 mmol) of compound **V** was added, the mixture was stirred for 5 h at 20°C, and the colorless precipitate was filtered off and washed with a small amount of trifluoroacetic anhydride. The product, 1,4,5,6,7-pentanitro-2,3-dihydro-1*H*-benzimidazol-2-one (**XV**), decomposed in 1 min on exposure to air at room temperature to 4,5,6,7-tetranitro derivative **V** (according to the HPLC data) with liberation of nitrogen oxides. The complete transformation of compound **XV** into **V** upon drying under reduced pressure over NaOH required approximately 5–6 days. Yield of **V** 0.68 g. Compound **XV** is unstable to the action of water, polar nonaqueous solvents, and anhydrous carboxylic acids and their anhydrides; therefore, we failed to obtain its satisfactory ^{1}H and ^{15}N NMR spectra.

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