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

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Abstract—*N*-Nitrobenzimidazol-2-ones readily undergo rearrangement to *C*-nitro derivatives on heating in various solvents (ethyl acetate, butyl acetate, acetonitrile, acetone, dioxane, *o*-dichlorobenzene, anisole, acetic acid). This rearrangement was used to develop a procedure for the synthesis of 4,5,6,7-tetranitro-1,3-dihydrobenzimidazol-2-one in high yield (90–96%) by nitration of 1,3-dihydrobenzimidazol-2-one, as well as of 5,6-dinitro- and 4,5,6-trinitro-1,3-dihydrobenzimidazol-2-ones, with a small excess of concentrated nitric acid in a mixture with acetic anhydride and acetic acid at 50–60°C.

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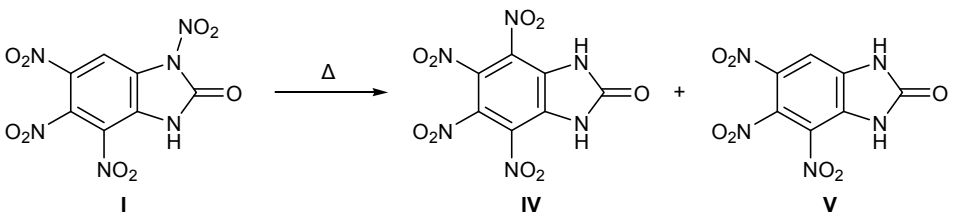
In the preceding communication [1] we reported on the synthesis of hitherto unknown 1,4,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**I**), 1,3,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**II**), and 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**III**). In continuation of our studies in this line, in the present work we examined some chemical transformations of *N*-nitro compounds **I**–**III**, namely their rearrangement into the corresponding *C*-nitro derivatives, which occurred on heating in various organic solvents.

Acid-catalyzed rearrangement of aromatic *N*-nitro amines (Bamberger rearrangement) involving migration of nitro group from nitrogen atom to the aromatic ring was the subject of numerous studies [2, 3]. Another version of such intramolecular rearrangement, so-called thermal rearrangement in *N*-nitro compounds, has been studied to a lesser extent. This reaction was reported in a few publications where rearrangements of some *N*-nitro derivatives of imidazole [4, 5], 1,2,4-triazole [6, 7], pyrazole [8–10], and indazole [11] were described. This rearrangement is performed in practice by prolonged heating of a solution of an *N*-nitro compound in a high-boiling solvent, such as anisole, nitrobenzene, toluene, or chlorobenzene, at a temperature above 110°C. As a result, the corresponding *C*-nitro derivatives are formed in high yields. The thermal rearrangement is an irreversible intramolecular first-order reaction [5, 6, 9–11]. Its mechanism is likely to involve [1,5]-sigmatropic migration of nitro group, followed by fast tautomerization.

We have found that analogous rearrangement of *N*-nitrobenzimidazol-2-ones **I**–**III** occurs under considerably milder conditions. In such solvents as acetone and acetonitrile, slow rearrangement of **I**–**III** is observed even at room temperature.

The rearrangement of 1,4,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**I**) on heating in organic solvents was most selective: the products were 4,5,6,7-

Scheme 1.



I **IV** **V**

* For communication I, see [1].

Table 1. Rearrangement of 1,4,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**I**) in different solvents

Solvent	Temperature, °C	Reaction time, h	Product composition,[a] mol %	
			V	**IV**
Acetic acid	55	5	13.0	87.0
Methanol	50	3	86.0	14.0
Isopropyl alcohol	50	3	97.5	2.5
Ethyl acetate	65	2	9.0	91.0
Ethyl acetate–dichloroethane (1 : 1)	65	2	7.0	93.0
Acetonitrile	80	0.5	25.0	75.0
Anisole[b]	75	1	98.0	2.0
Dioxane[b]	100	0.5	77.0	23.0
Acetone	55	0.5	23.0	77.0
o-Dichlorobenzene[b]	100	0.5	95.0	5.0
Butyl acetate	126	0.1	25.0	75.0
Butyl acetate	65	3	7.0	93.0
Toluene[b]	110	0.2	100	0

[a] According to the HPLC data.
[b] Compound **I** is poorly soluble in these solvents.

tetranitro and 4,5,6-trinitro derivatives **IV** and **V** whose ratio depended on the conditions (Scheme 1, Table 1).

As might be expected, 1,3,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**II**) under analogous conditions gave rise to a mixture of denitration product, 5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**VI**), with compounds **V** and **IV**, the latter prevailing (Scheme 2, Table 2). A mixture of compounds **IV**–**VI** was also formed in the rearrangement of 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**III**), e.g., in butyl acetate (Scheme 3, Table 2). This unexpected result indicates that the rearrangement of *N*-nitrobenzimidazolones cannot be regarded as strictly intramolecular.

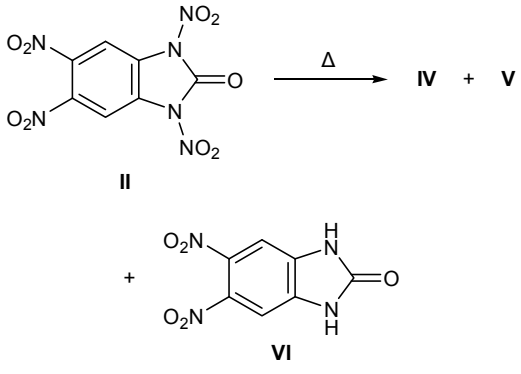
Some general relations were revealed while studying the rearrangement should be noted. The yield of *C*-nitro compounds **IV** and **V** increases in parallel with the number of nitro groups in the initial *N*-nitro derivative. Presumably, the process follows a radical pattern where the rate-determining step is homolytic dissociation of the N–N bond in initial *N*-nitro compound. The data in Tables 1 and 2 show that the denitration product is formed with the largest yield by rearrangement of the least strained 1,5,6-trinitro derivative **III**; under analogous conditions, tetranitro derivatives **I** and **II**

Table 2. Rearrangements of 1,3,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**II**) and 1,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**III**) in butyl acetate at 70°C (reaction time 3 h)

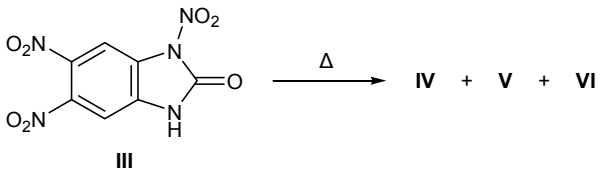
Initial compound no.	Product composition,[a] mol %		
	IV	**V**	**VI**
II	63.4	28.4	8.2
III	5	50	45

[a] According to the HPLC data.

Scheme 2.



Scheme 3.

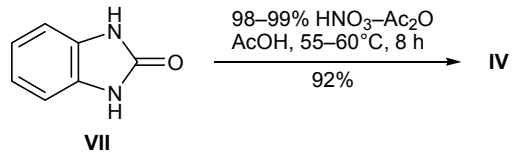


give rise to higher yield of *C*-nitro derivatives. The *N*-nitro group in 1,3,5,6-tetranitrobenzimidazolone **II** is the most reactive. Unlike compounds **I** and **III**, dissolution of 1,3,5,6-tetranitro derivative **II** in ethanol is accompanied by elimination of one *N*-nitro group with quantitative formation of compound **III** (the reaction is complete in 1 min). For comparison, complete N-denitration of 1,4,5,6-tetranitrobenzimidazolone **I** in ethanol at room temperature requires 36 h.

It is not advisable to carry out the rearrangement in a boiling solvent even if its boiling point is not high. Elevated temperature is likely to favor denitration of *N*-nitrobenzimidazolones. Poor solubility of *N*-nitro compound **I** in high-boiling aromatic solvents (anisole, *o*-dichlorobenzene, toluene) is a factor favoring denitration, and the major product is 4,5,6-trinitrobenzimidazolone **V**.

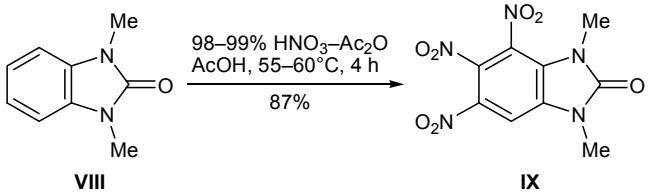
The yield of compound **IV** in the rearrangement of 1,4,5,6-tetranitrobenzimidazolone **I** in acetic acid was unexpectedly high. This prompted us to develop a procedure for the synthesis of 4,5,6,7-tetranitro derivative **IV** by nitration of 5,6-dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**VI**) or 4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**V**) under mild conditions appropriate for both nitration at the nitrogen atom and N→C migration of the nitro group in *N*-nitrobenzimidazolone derivatives. We examined nitration of compounds **V** and **VI** with nitric acid in acetic anhydride (HNO_3–Ac_2O molar ratio 1 : 1) with addition of acetic acid at 50–60°C. The nitration of 5,6-dinitrobenzimidazolone **VI** with nitric acid (4.5 mol of HNO_3 per mole of **VI**; reaction time 5 h) at 55°C gave 4,5,6,7-tetranitro derivative **IV** in 96% yield, while the fraction of 4,5,6-trinitrobenzimidazolone **V** was less than 0.3 mol %. Analogous results were obtained in the nitration of compound **V**. Larger amount of nitric acid was necessary for the nitration of 2,3-dihydro-1*H*-benzimidazol-2-one (**VII**) to 4,5,6,7-tetranitro derivative **IV**; in this case, compound **IV** was formed in 92% yield (Scheme 4).

Scheme 4.



1,3-Dimethyl-2,3-dihydro-1*H*-benzimidazol-2-one (**VIII**) is a compound for which the rearrangement under study is impossible. The nitration of **VIII** under analogous conditions (HNO_3–Ac_2O molar ratio 1 : 1, AcOH) afforded 87% of 1,3-dimethyl-4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**IX**) (Scheme 5).

Scheme 5.



It is known that [12–17] aromatic *N*-nitro amines, such as *N*-nitroaniline and *N*-nitropyridin-2-amine, in aqueous solutions of strong acids undergo rearrangement involving migration of the nitro group into the aromatic ring. The major products of this rearrangement are the corresponding *ortho*-nitro derivatives, though some amounts of *para*-nitro derivatives were also detected. The yield of the rearrangement products exceeds 95% at high acidity of the medium. Low acid concentration favors tarring. The authors presumed [12–17] that the rearrangement is intramolecular.

According to the HPLC data, dissolution of 1,3,5,6-tetranitrobenzimidazolone **II** in 93% H_2SO_4 at room temperature is accompanied by its fast (within ~1 min) disappearance, and the concentration of the corresponding *C*-nitro derivatives, 4,5,6-trinitrobenzimidazolone **V** and 4,5,6,7-tetranitrobenzimidazolone **IV** gradually increases (Table 3). These findings suggest that the rearrangement is not intramolecular. Presumably, the initial step is fast denitration of 1,3,5,6-tetranitrobenzimidazolone **II**, and next follows nitration of the denitrated product with 2 equiv of HNO_3.

To conclude, we showed that *N*-nitrobenzimidazolones **I**–**III** readily undergo rearrangement into the corresponding *C*-nitro derivatives on heating in various organic solvents (ethyl acetate, butyl acetate, acetonitrile, acetone, dioxane, *o*-dichlorobenzene, anisole). The ease of this rearrangement allowed us to develop a procedure for the synthesis of 4,5,6,7-tetranitro-2,3-

Table 3. Transformation of 1,3,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (**II**) in 93% sulfuric acid at 20–25°C

Reaction time, h	Product composition,[a] mol %		
	IV	**V**	**VI**
1	–	13	87
24	–	63	37
72	1.30	98.54	0.16

[a] According to the HPLC data.

dihydro-1*H*-benzimidazol-2-one (**IV**) in high yield (90–96%) by nitration of benzimidazol-2-one (**VII**), 5,6-dinitrobenzimidazolone **VI**, and 4,5,6-trinitrobenzimidazolone **V** using a small excess of concentrated nitric acid in a mixture with acetic anhydride and acetic acid at 50–60°C.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu FTIR 8400 spectrometer from samples prepared as KBr pellets. The ^{1}H 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 reaction mixtures were analyzed by HPLC on a Milikhrom liquid chromatograph equipped with a spectrophotometric detector (working wavelength λ 250 nm); Silasorb C18 column (LaChema, Czechia), 63 mm×2 mm, grain size 5 μm; eluent water–acetonitrile–acetic acid, 100:22:1 (by weight), flow rate 100 μl/min; sample volume 2–4 μl. Listed below are compound no. and retention time, s: **VI**, 243; **V**, 380, **I**, 485; **III**, 569; **IV**, 957. The components were quantitated by the internal normalization technique using calibration factors.

5,6-Dinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**VI**) and 4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (**V**) were synthesized according to the procedures described in [1, 18].

1,4,5,6-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (I). Acetic anhydride, 8 ml, was added at 20–25°C to 7 ml of 98–99% nitric acid, and 1 g (3.7 mmol) of compound **V** was added in small portions under stirring. 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 (C–NO_2), 1484 (C=C), 1446, 1398 (C=C), 1345 (C–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). 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.

1,3,5,6-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (II). Acetic anhydride, 50 ml, was added at 20–25°C to 50 ml of 98–99% nitric acid, 7 g (31.2 mmol) of compound **VI** was added in small portions, and the mixture was kept 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 6.6 g (67%), colorless crystals, mp 120–121°C (decomp.). IR spectrum, ν, cm^{-1}: 3390, 3135 (CH), 2887 (CH), 1818 (CH), 1633 (C=O), 1606 (C=O, C=C), 1543 (C–NO_2), 1470 (C=C), 1385 (C=C), 1361 (C–NO_2), 1267 (N–NO_2), 1232, 1143 (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 (2H). 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.

1,5,6-Trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (III). 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 **VI** was added in small portions at such a rate that the temperature did not exceed 20°C. The mixture was kept 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.) IR spectrum, ν, cm^{-1}: 3362 (NH), 3164 (CH), 3133 (CH), 3078 (CH), 1773 (CH), 1629 (C=O), 1593 (C=O, C=C), 1546 (C–NO_2), 1487 (C=C), 1460 (C=C), 1339 (C–NO_2), 1253 (N–NO_2), 1170 (NH), 1079 (N–N), 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.

Rearrangement of *N*-nitrobenzimidazolones I–III into *C*-nitro compounds (*general procedure*). A mixture of 0.1 g of *N*-nitrobenzimidazolone **I**–**III** and 10 ml of appropriate solvent was heated as long as necessary at a required temperature. The mixture was then cooled to 20–25°C and evaporated, and the solid residue was analyzed by HPLC. For reaction conditions and product yields, see Tables 1 and 2.

Transformation of 1,4,5,6-tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (I) in 93% sulfuric acid. A solution of 1 g (3.2 mmol) of compound **I** in 10 ml of 93% sulfuric acid was stirred for a required time at room temperature. The mixture was poured into 100 ml of cold water, and the precipitate was filtered off, washed with water, and dried in air. The product composition and ratio were determined by HPLC (Table 3).

4,5,6,7-Tetranitro-2,3-dihydro-1*H*-benzimidazol-2-one (IV). *a*. Acetic anhydride, 5 g (49.0 mmol), and

acetic acid, 5 g (83.3 mmol), were mixed at 20–25°C with 3 g (46.6 mmol) of 98–99% nitric acid, 2 g (8.9 mmol) of 5,6-dinitrobenzimidazolone **VI** was added, and the mixture was stirred for 5 h at 55°C, cooled to room temperature, and poured into 150 ml of water. The precipitate was filtered off, thoroughly washed with water, and dried at 80°C. According to the HPLC data, the crude product contained 0.3 mol % of 4,5,6-trinitrobenzimidazolone **V** as impurity. Yield 2.7 g (96%), bright yellow crystals, mp 317–319°C (decomp.). IR spectrum, ν, cm^{-1}: 3401 (NH), 3138 (C–N, C_{arom}), 1752 (C_{arom}), 1618 (C=O, C=C), 1550 (NO_2), 1501 (C=C), 1400 (C=C), 1339 (NO_2), 1206 (NO_2), 1054, 987, 931, 911, 864 (C–H_{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.

b. 4,5,6-Trinitrobenzimidazolone **V**, 2 g (7.7 mmol), was added to acid mixture prepared as described above in *a*. The mixture was stirred for 6 h at 60°C, cooled to room temperature, and poured into 150 ml of water, and the precipitate was filtered off, thoroughly washed with water, and dried at 80°C. Yield 2.1 g (90%), bright yellow crystals, mp 318–319°C (decomp.).

c. Acetic anhydride, 13 g (127.3 mmol), and acetic acid, 8 g (133.3 mmol), were mixed at 20–25°C with 7.6 g (118.2 mmol) of 98–99% nitric acid, 2.7 g (20.1 mmol) of 2,3-dihydro-1*H*-benzimidazol-2-one (**VII**) was added, and the mixture was stirred for 8 h at 55–60°C, cooled to room temperature, and poured into 250 ml of water. The precipitate was filtered off, thoroughly washed with water, and dried at 80°C. According to the HPLC data, the crude product contained 3 mol % of 4,5,6-trinitrobenzimidazolone **V** as impurity. Yield 5.8 g (92%), bright yellow crystals, mp 316–317°C (decomp.).

1,3-Dimethyl-4,5,6-trinitro-2,3-dihydro-1*H*-benzimidazol-2-one (IX). Acetic anhydride, 13 g (127.3 mmol), and acetic acid, 8 g (133.3 mmol), were mixed at 20–25°C with 7.6 g (118.2 mmol) of 98–99% nitric acid, 2.5 g (15.4 mmol) of 1,3-dimethyl-2,3-dihydro-1*H*-benzimidazol-2-one (**VIII**) was added, and the mixture was stirred for 4 h at 55–60°C, cooled to room temperature, and poured into 250 ml of water. The precipitate was filtered off, thoroughly washed with water, and dried at 80°C. Yield 4.0 g (87%), yellow crystals, mp 202–204°C (decomp.; from EtOH). IR spectrum, ν, cm^{-1}: 3473, 3099 (C–H_{arom}), 3070 (C–H_{arom}), 2960, 2893 (CH_3), 1741 (C_{arom}), 1621 (C=O, C=C), 1611 (C=O, C=C), 1547 (NO_2), 1511 (C=C), 1462, 1428 (C=C), 1357 (NO_2), 1334, 1265, 1238 (NO_2), 1170, 1115, 993, 923, 858 (δC–H_{arom}), 817, 779, 769, 755, 743, 668, 574. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.32 s (3H, CH_3), 3.52 s (3H, CH_3), 8.41 s (1H, 7-H). Found, %: C 36.26; H 2.58; N 23.74. $C_9H_7N_5O_7$. Calculated, %: C 36.37; H 2.37; N 23.57.

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