Nitrolysis of 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane

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Nitrolysis of 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{3,11}.0^{5,9}]dodecane results in the substitution of benzyl groups by the nitro groups with the formation of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]-dodecane. The reaction sequentially proceeds through the nitration of the benzyl groups predominantly at *para*-position, the substitution of one nitrobenzyl group with the nitro group, and the introduction of the second nitro group into the nitrobenzyl fragment. The replacement of the remaining dinitrobenzyl fragment is a more difficult process, which reaches completion only by the end of the nitration. Another reaction product is *p*-nitrobenzoic acid, which is formed in the secondary reactions. No substitution of a *p*-nitrobenzoyl group with the nitro group takes place in the nitration of 2,6,8,12-tetraacetyl-4,10-di(*p*-nitrobenzoyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane under similar conditions.

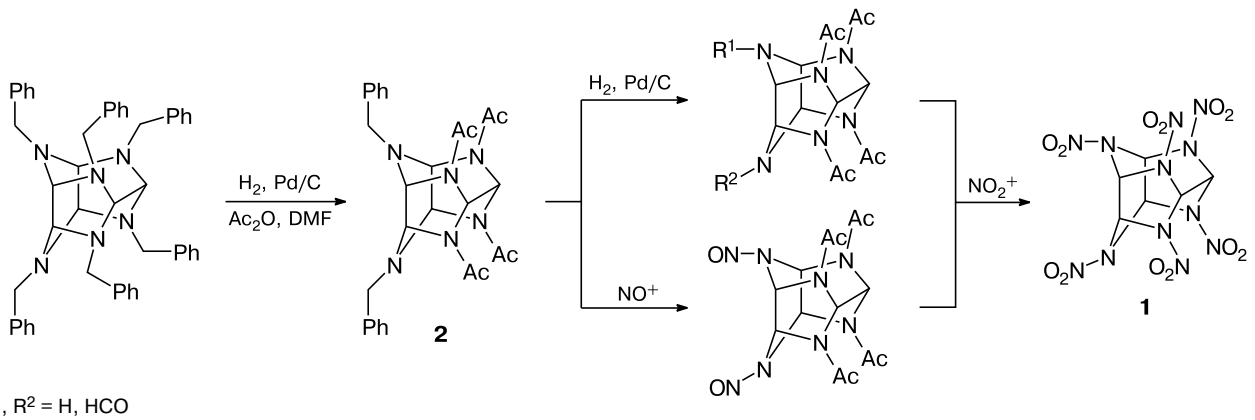
Key words: 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]-dodecane, nitrolysis, *N*-nitro compounds.

The intermediate compound in synthesis of one of the highly energetic compounds, namely, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]-dodecane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, CL-20, HNIW) (**1**), is 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{3,11}.0^{5,9}]dodecane (**2**).[1—3] It is obtained by debenzylation and subsequent acylation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]-dodecane in the mixture of DMF and Ac_2O.[1—4] The remaining benzyl groups in compound **2** are removed by hydrogenation[3,5,6] or nitrosation[2,7] and only then the nitration is applied (Scheme 1).

At the same time, we have demonstrated a possibility of the substitution of a benzyl group in compound **2** with the nitro group upon treatment with nitrating mixtures based on nitric acid[8] (Scheme 2). The nitrolysis of **2** in the system NH_4NO_3—HNO_3 at 100—118 °C gave a mixture of compound **1** with *p*-nitrobenzoic acid.

The nitration of **2** at a temperature below 0 °C leads to 2,6,8,12-tetraacetyl-4,10-di(nitrobenzyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**3**). In this

Scheme 1



R^1, R^2 = H, HCO

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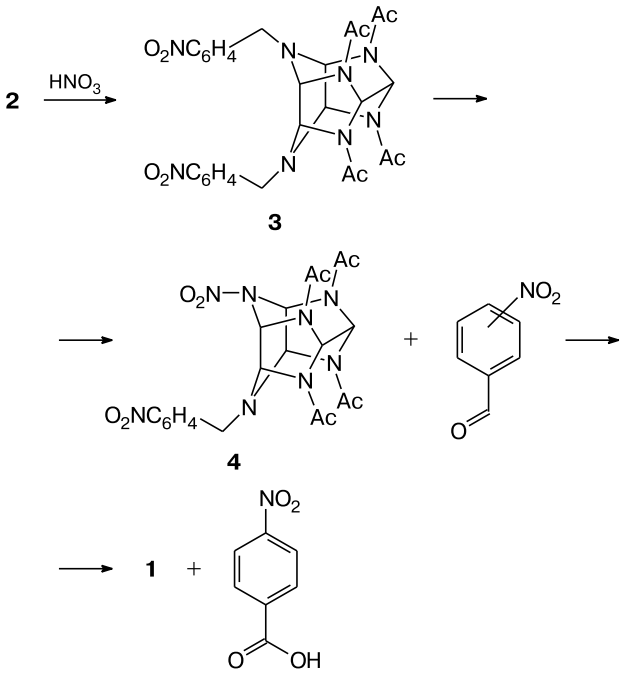
Scheme 2



case, the NMR spectroscopy data showed that a mixture of isomers of compound **3** was formed The HPLC results indicate the presence of four out of six possible isomers of compound **3** in the ratio of 3.5 : 14.3 : 22.0 : 60.2. The highest yield of **3** (63.8%) was obtained in the nitration over 1 h at −30 °C. The elevation of temperature to 0 °C leads to the formation of 2,6,8,12-tetraacetyl-4-nitro-10-*p*-nitrobenzyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{3,11}.0^{5,9}]dodecane (**4**) as an impurity, which was isolated by preparative chromatography.

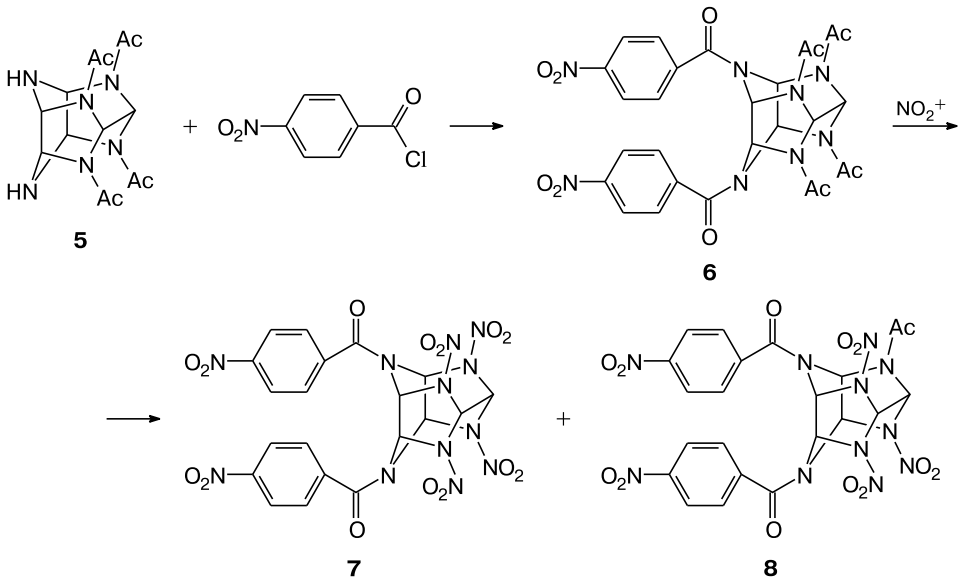
The easiness of the formation of **3** indicates that initially the benzyl groups are predominantly nitrated at *para*-position. The next step of the process can be a direct replacement of a *p*-nitrobenzyl group with the nitro group. However, because of the formation of a considerable amount of nitrobenzoic acid in the process of nitration (together with **1**), a possibility of oxidation of a nitrobenzyl group to the nitrobenzoyl one with its subsequent substitution cannot be excluded.

To check this suggestion, 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**5**) was acylated with *p*-nitrobenzoyl chloride to 2,6,8,12-tetraacetyl-4,10-di(*p*-nitrobenzoyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**6**) (Scheme 3).

The nitrolysis of **6** under conditions for obtaining **1** leads to 4,10-di(*p*-nitrobenzoyl)-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**7**) in 69% yield. Compound **1** was formed only as an impurity, in the yield, according to the HPLC data, not exceeding 2%. Another impurity, isolated by preparative column chromatography, was identified as a product of the incomplete nitration, namely, 2-acetyl-4,10-di(*p*-nitrobenzoyl)-6,8,12-trinitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**8**).

When the temperature of nitration of **2** was increased to ambient, one of the nitrobenzyl group quite readily undergoes substitution. Thus, the nitration in a mixture of NH_4NO_3—HNO_3 (1 : 4, w/w) already after 5 h of standing at room temperature leads to a mixture of **4**, nitrobenzaldehyde, and a small amount of a mixture of products of deeper nitration (their nitration leads to **1**). An increase in the reaction time to 24 h practically does not affect the content of the products: the yields of **4** and nitrobenzaldehyde isomers were 93.6% and 84.2%, respectively. It can

Scheme 3



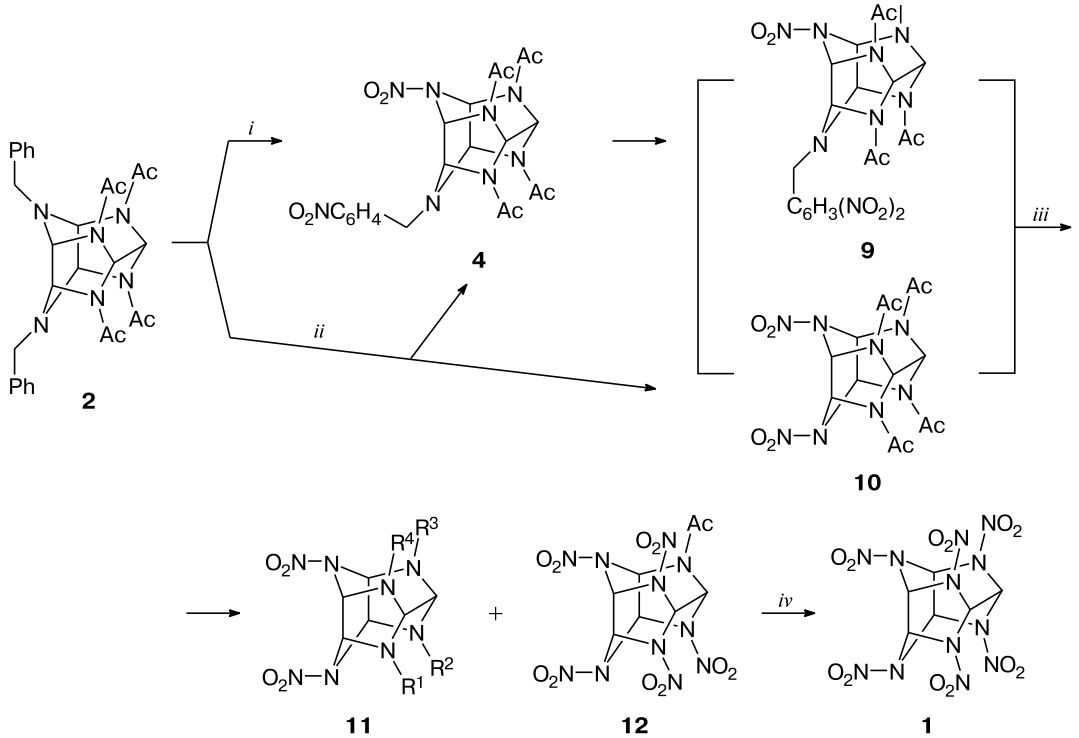
be suggested that in the process of nitration, the elimination of a nitrobenzyl cation takes place, which stabilizes by conversion to nitrobenzyl nitrate and then oxidizes to nitrobenzaldehyde. Analysis of **4** by HPLC showed the presence of three main products with close retention times and with the content of 22.6%, 9.0%, and 68.4%. The ^{1}H NMR spectrum of the mixture contains a group of peaks in the region of δ_H 7.6—8.8, which, taking into account the ^{13}C NMR spectra, can be assigned to the signals of the mixture of isomeric nitrobenzyl groups. The integral sum of the peaks for the aromatic protons corresponds to the structure of a mixture of isomers of **4**. The crystallization of the product from nitromethane increased the content of *para*-nitrobenzyl derivative of **4** to 85%.

The GLC analysis of the content of nitrobenzaldehydes showed the following percentage of isomers: 6.8% (*ortho*), 34.0% (*meta*), 59.1% (*para*). It is obvious that the isomeric composition of the obtained nitrobenzaldehyde characterizes the presence of a nitro group during nitration of the benzyl groups in the starting **2** and almost corresponds to the composition **3** and **4**. Note that in the nitration of **2** in the AcOH—HNO_3 mixture, a nitrobenzyl group also undergoes replacement with the nitro group, and in this case the content of *ortho*-, *meta*-, and *para*-isomers of nitrobenzaldehyde was 18.9, 37.54, and 43.55%, respectively. These results allow us to state that the position of the nitro groups in the intermediate product **3** has little effect on subsequent replacement of a nitrobenzyl group with the nitro group.

The nitration of **2** at room temperature with nitric acid (without NH_4NO_3) proceeds slightly deeper (Scheme 4). Thus, for example, the product isolated after 24 h contained a mixture of nitrobenzaldehydes, 2,6,8,12-tetraacetyl-4-nitro-10-nitrobenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (**4**), 2,6,8,12-tetraacetyl-4-nitro-10-dinitrobenzyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{3,11}.0^{5,9}]dodecane (**9**), 2,6,8,12-tetraacetyl-4,10-dinitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]-dodecane (**10**) and a small amount of unidentified products. In the case of nitration of **4**, the 4-nitro-10-dinitrobenzyl derivative **9** became a predominant product. The main out of possible isomers of **9**, namely 2,6,8,12-tetraacetyl-10-(2,4-dinitrobenzyl)-4-nitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane, was isolated in the pure state by preparative chromatography.

The nitration of **4** at 110—118 °C leads to a mixture of **1** with *p*-nitrobenzoic acid. The reprecipitation of the product from aqueous alcohol gave pure **1** in 60.5% yield. At the same time, the nitration of **9** gave **1** in 57.2% yield with the content of the main compound 96.5%. 2,4-Di-

Scheme 4



A mixture of isomers R^1, R^2, R^3, R^4 = Ac, Ac, NO_2, NO_2.

Reagents and conditions: *i*. HNO_3, NH_4NO_3, 20 °C, 24 h; *ii*. HNO_3, 20 °C, 24 h; *iii*. HNO_3, NH_4NO_3, 78 °C, 7 h; *iv*. HNO_3, NH_4NO_3, 95—110 °C.

nitrobenzoic acid was isolated in 31% yield. When the temperature of the nitration of **4** was decreased to 77—79 °C (7 h), compound **1** was formed only as an impurity, HPLC showed the presence of the starting compound **4**, compounds **9**—**11**, and a number of other products. The products of nitration of **4** at 95 °C (7 h) contain approximately 40.4% of **1**, 10.6% of **11**, and 19.4% of **12**.

The obtained results indicate that a complete removal of the aromatic fragment in the nitrolysis of **2** required the reaction temperature higher 95 °C and proceeded simultaneously with the substitution of acetyl groups with the nitro groups. However, even under these conditions the mixture of nitration products with the presence of no more than two acetyl groups (a mixture of **1**, **11**, and **12**) contains a component with the nitro- or dinitrobenzyl fragment as an impurity. Apparently, a relatively low stability of the isowurtzitane with a benzyl group in the acidic medium causes destruction of the product and, therefore, a moderate yield of **1** (no more than 60%) in the nitration of **2**. To sum up, the nitrolysis of **2** to **1** proceeds through the initial formation of di(nitrobenzyl) derivative **3**, with subsequent replacement of one of the nitrobenzyl groups with the nitro group. Then, several parallel processes take place: the replacement of a remaining nitrobenzyl group with the nitro group; its nitration to dinitrobenzyl group; substitution of acetyl groups with the nitro groups, while the benzyl fragment in **2** is completely removed only at the end of the nitrolysis. *para*-Nitrobenzoic acid is formed as a result of secondary reactions (oxidation). No substitution of a *p*-nitrobenzoyl group with the nitro group under similar conditions in the nitration of 2,6,8,12-tetraacetyl-4,10-di(*p*-nitrobenzoyl)-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.$0^{3,11}$.$0^{5,9}$]dodecane (**6**) occurs.

Experimental

IR spectra of compounds were recorded on a Infralyum FT-801 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.13 (^{1}H) and 100.61 MHz (^{13}C), using DMSO-d_6 as the solvent. HPLC was carried out on an Agilent 1200 instrument; a 2.1×15-mm preliminary column, sorbent Zorbax SB-18, 3 μm; a 2.1×150-mm column, sorbent Zorbax SB-18, 5 μm. The content and the quality of products were determined by a UV detector (λ = 230 nm) using gradient elution. Eluent A: 0.2% solution of orthophosphoric acid, eluent B: acetonitrile. TLC was carried out on Merck Silica gel 60 F_{254} plates. Preparative chromatography was carried out on a column (700×12 mm) with Merck silica gel (0.063—0.2-mm fraction). Elemental analysis was carried out on a FlashEA^{TM} 1112 elemental C,H,N,O-analyzer. GLC-analysis was carried out on a Khromos GKh-1000 chromatograph with a flame-ionizing detector, a 4×2000-mm chromatographic column, sorbent 5% XE-60 Inerton-Super, 0.16—0.2 mm, injector temperature 220 °C, thermostat temperature 130 °C, the rate of carrier gas (nitrogen) 24 mL min^{-1}, the rate of hydrogen 20 mL min^{-1}, the rate of air 200 mL min^{-1}.

Compounds **2** and **5** were obtained by hydrogenolysis of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane.[3,5]

2,4,10,6,8,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.$0^{3,11}$.$0^{5,9}$]dodecane (1). ***A.*** A 99% HNO_3 (21 mL, 0.5 mol) and NH_4NO_3 (10.5 g, 0.13 mol) were placed into a three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser. Then, compound **2** (6.0 g, 11.6 mmol) was added at a temperature about 20 °C. The reaction mixture was allowed to stand for 1 h, then heated to reflux over 1 h, and maintained over 8 h at 100—118 °C. Then, it was cooled, diluted with a mixture of ice with water (150 g), a precipitate was filtered off, washed with water, and dried in air. Then, the precipitate was dissolved in acetone (25 mL) with heating and poured into a mixture of EtOH (50 mL) and water (150 mL) at 60—80 °C with stirring. The resulting suspension was stirred for 1 h and filtered hot. The product was washed with 20% aqueous EtOH (2×20 mL) and dried in air to obtain compound **1** (1.8 g, 35.4%) with a decomposition temperature of 242—250 °C. The results of elemental analysis, IR and ^{1}H NMR spectroscopy corresponded to those described in the literature.

B. A 99% HNO_3 (23 mL, 0.55 mol), compound **4** (6.2 g, 12 mmol), and NH_4NO_3 (11.0 g, 0.137 mol) were placed into a three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser with cooling by an ice-cold water. The reaction mixture was allowed to stand over 30 min without cooling and heated to reflux over 1 h. Then, the mixture was refluxed until the temperature raised to 120 °C (10 h), cooled, and diluted with a mixture of water with ice (150 g), a precipitate was filtered, washed with water (5×15 mL), and dried in air to obtain the product (4.03 g). The product was dissolved in acetone (35 mL) and reprecipitated by pouring into the mixture of EtOH (100 mL) and water (300 mL) as described earlier to obtain compound **1** (3.18 g, 60.5%) with the content of the main substance of 99.2%.

C. A 99% HNO_3 (20 mL, 0.48 mol), compound **9** (4.2 g, 7.5 mmol), and NH_4NO_3 (9.5 g, 0.119 mol) were placed into a three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser with cooling by an ice-cold water. The reaction mixture was allowed to stand for 30 min without cooling and heated to reflux over 1 h. Then, the mixture was refluxed until the temperature raised to 118 °C, cooled, and diluted with a mixture of water with ice (150 g). A precipitate was filtered, washed with water (5×15 mL), and dried in air to obtain compound **1** (1.95 g) with the content of the main substance of 96,5%. The reprecipitation of **1** from a solution of acetone (15 mL) into a mixture of EtOH (50 mL) and water (150 mL) gave **1** (1.88 g, 57.2%) with a 98.8% content of the main compound.

2,6,8,12-Tetraacetyl-4,10-di(nitrobenzyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.$0^{3,11}$.$0^{5,9}$]dodecane (3). ***A.*** Compound **2** (6 g, 11.6 mmol) was added in small portions into a three-neck flask equipped with a stirrer and a thermometer containing 99% HNO_3 (30 mL, 0.71 mol) and cooled to −30 °C (liquid nitrogen—$CHCl_3$) and the mixture was allowed to stand at this temperature for 1 h. Then, the reaction mixture was diluted with ice-cold water (500 mL). A precipitate was washed with ice-cold water (with decantation), filtered off, and washed with water. After drying in air, the precipitate was treated with MeCN at 40—45 °C. The product was filtered off, washed with MeCN (8 mL), and dried in air to obtain compound **3** (3.6 g). According to the HPLC data, the product was a mixture of isomers with the ratio of 3.5 : 14.3 : 22.0 : 60.2.

The analytically pure sample of the product was obtained by five-time recrystallization from MeCN, which gave compound **3** with a 94% content of the main isomer.

M.p. 262—272 °C (from acetonitrile). Found (%): C, 55.45; H, 5.16; N, 18.39. $C_{28}H_{30}N_8O_8$. Calculated (%): C, 55.44; H, 4.98; N, 18.47. IR, ν/cm^{-1}: 3077, 3044, 3017, 2917, 2863, 1661, 1605, 1517, 1395, 1347, 1290, 1259, 1131, 1038, 995, 853, 813, 773, 699, 629, 547. ^{1}H NMR, δ: 1.91—2.11 (m, 12 H, CH_3CO); 4.08—4.25 (m, 4 H, CH_2); 5.33—5.56 (m, 4 H, CH); 6.25—6.68 (m, 2 H, CH); 7.79 (br.s, 4 H, Ar); 8.27 (d, 4 H, Ar, J = 10.4 Hz). ^{13}C NMR, δ: 20.70, 21.98 ($\underline{C}H_3CO$); 54.14, 54.75 (CH_2); 68.14, 68.62, 69.76, 70.72, 71.49, 72.67 (CH); 123.38, 129.36, 129.89 (CH, Ar); 146.76, 146.92 (C, Ar); 167.04, 167.99, 168.08 ($CH_3\underline{C}O$).

B. Glacial AcOH (14 mL) and Ac_2O (8 mL) were placed into a three-neck flask equipped with a stirrer and a thermometer, followed by the addition of 99% HNO_3 (4 mL) with cooling in an ice-water bath. Compound **2** (4.6 g) was added to the prepared nitration mixture cooled to 0 °C and this was allowed to stand for 3 h at 0 °C. Then, the reaction mixture was poured into a mixture of ice with water (300 g). A precipitate was filtered off, washed with water, and dried in air. The product was treated with Me_2CO (35 mL), after 2 h filtered off, washed with Me_2CO, and dried in air to obtain a precipitate (1.5 g). An additional amount of the precipitate (0.7 g) was isolated by the concentration of Me_2CO. The TLC data showed that the combined precipitate contained two main products; 0.7 g of the precipitate was dissolved in MeCN and separated by preparative chromatography, eluent MeCN : MeOH (10 : 1, v/v). Two main products were isolated: the sample (0.28 g, 16.0%) with R_f = 0.33 (TLC), the IR and NMR spectra and the results of elemental analysis of which were similar to those for compound **3** obtained earlier; the sample (0.15 g, 10.0%) with R_f = 0.56 (TLC) corresponding to compound **4**.

2,6,8,12-Tetraacetyl-4-nitro-10(*p*-nitrobenzyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (4). M.p. 260—265 °C. Found (%): C, 49.03; H, 4.51; N, 21.62. $C_{21}H_{24}N_8O_8$. Calculated (%): C, 48.84; H, 4.68; N, 21.70. IR, ν/cm^{-1}: 3020, 2920, 2845, 1665, 1600, 1550, 1520, 1395, 1345, 1290, 1255, 1160, 1125, 1038, 945, 887, 855, 773, 725, 629, 547. ^{1}H NMR, δ: 2.07—2.14 (m, 12 H, CH_3CO); 4.08—4.28 (m, 2 H, CH_2); 5.57—5.90 (m, 2 H, CH); 6.47—7.75 (m, 4 H, CH); 7.49 (d, 2 H, Ar, J = 10.8 Hz); 8.20 (d, 2 H, Ar, J = 11.4 Hz). ^{13}C NMR, δ: 20.56, 50.70, 21.72 ($\underline{C}H_3CO$); 54.91 (CH_2); 67.15, 68.86, 69.71, 70.41, 71.6, 73.4 (CH); 123.30, 129.62 (CH, Ar); 145.78, 146.99 (C, Ar); 166.80, 168.20 ($CH_3\underline{C}O$).

2,6,8,12-Tetraacetyl-4,10-di(*p*-nitrobenzoyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (6). 2,6,8,12-Tetraacetyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (6.0 g, 0.017 mol), anhydrous MeCN (70 mL), and *p*-nitrobenzoyl chloride (26 g, 0.14 mol) were placed into a flat-bottom flask. The flask was placed on a magnetic stirrer and refluxed with a refluxed condenser for 7 h. The resulting solution was concentrated on a rotary evaporator. The residue was treated with EtOH (150 mL). The product was filtered off, washed with EtOH (2×30 mL), and dried in air. Compound **6** (7.0 g, 0.012 mol, 66.7%) was obtained after crystallization from a mixture of EtOH—MeCN (280 mL, 7 : 3, v/v). M.p. 268—272 °C (from a mixture of EtOH—MeCN). Found (%): C, 52.3; H, 4.18; N, 17.53. $C_{28}H_{26}N_8O_{10}$. Calculated (%): C, 53.00; H, 4.13; N, 17.66. IR, ν/cm^{-1}: 3109, 3043, 2917, 2863, 1678, 1603, 1525, 1402, 1355, 1305, 1142, 1053, 860, 767, 721, 706, 622, 515. ^{1}H NMR, δ: 2.02 (s, 6 H, CH_3CO); 2.14 (s, 6 H, CH_3CO); 6.21—7.05 (m, 6 H, CH); 7.85 (d, 4 H, Ar, J = 10.8 Hz); 8.38 (d, 4 H, Ar, J = 11.4 Hz). ^{13}C NMR, δ: 20.85, 21.91 ($\underline{C}H_3CO$); 63.55, 68.65, 71.60 (CH); 123.72, 129.33 (CH, Ar); 139.19, 148.75 (C, Ar); 167.65, 167.89 ($CH_3\underline{C}O$); 169.44 (CO).

Synthesis of compounds 7 and 8. A 99% HNO_3 (21 mL) and NH_4NO_3 (10.5 g) were placed into a three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser. Then, product **6** (6.1 g) was added to the obtained solution. The reaction mixture was allowed to stand for 8 h at 100—110 °C, cooled, and poured into a mixture of ice with water. A precipitate was filtered off, washed with water (6×10 mL), and dried in air to obtain a mixture of products (5.8 g). According to the HPLC data, the mixture contained 2% of compound **1**, 25% of compound **8**, and 70% of compound **3**. After crystallization from MeCN, a mixture of compounds **8** and **7** (4.4 g) was obtained. For analytical purposes, 0.7 g of the mixture was separated by preparative column chromatography. Eluent *o*-xylene : Me_2CO = = 7 : 1 (v/v). Two products were isolated: the sample (0.45 g) with R_f = 0.64 (TLC) corresponding to compound **7** and the sample (0.18 g) with R_f = 0.4 (TLC) corresponding to compound **8**.

4,10-Di(*p*-nitrobenzoyl)-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (7). M.p. 242—244 °C (decomp.). Found (%): C, 37.8; H, 2.09; N, 26.15. $C_{20}H_{14}N_{12}O_{14}$. Calculated (%): C, 37.16; H, 2.18; N, 26.00. IR, ν/cm^{-1}: 3112, 3026, 2923, 2858, 1690, 1619, 1601, 1567, 1526, 1402, 1352, 1310, 1264, 1182, 953, 863, 756, 699, 656, 571. ^{1}H NMR, δ: 6.75—7.90 (m, 6 H, CH); 7.93 (d, 4 H, Ar, J = 8 Hz); 8.46 (d, 4 H, Ar, J = 8 Hz). ^{13}C NMR, δ: 73.46 (CH); 124.00 (CH, Ar); 130.03 (CH, Ar); 137.61, 149.29 (C, Ar); 168.88 (C, $\underline{C}O$).

2-Acetyl-4,10-di(*p*-nitrobenzoyl)-6,8,12-trinitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (8). M.p. 226—228 °C. Found (%): C, 40.98; H, 2.49; N, 24.0. $C_{22}H_{17}N_{11}O_{13}$. Calculated (%): C, 41.07; H, 2.66; N, 23.95. IR, ν/cm^{-1}: 3111, 3034, 2921, 2852, 1691, 1603, 1556, 1527, 1398, 1353, 1311, 1266, 1175, 1105, 953, 863, 758, 701, 662, 571. ^{1}H NMR, δ: 2.16 (s, 3 H, CH_3CO); 6.45—7.72 (m, 6 H, CH); 7.89 (d, 4 H, Ar, J = 8 Hz); 8.45 (d, 4 H, Ar, J = 8 Hz). ^{13}C NMR, δ: 20.05 ($\underline{C}H_3CO$); 69.44 (CH); 124.06, 129.90 (CH, Ar); 137.89, 149.24 (C, Ar); 161.02, 168.2 (C, CO).

2,6,8,12-Tetraacetyl-4-nitro-10(*p*-nitrobenzyl)-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (4). A 99% HNO_3 (53 mL) and NH_4NO_3 (20.0 g) were placed into a three-neck flask equipped with a stirrer and a thermometer. Product **2** (10.0 g) was added to the obtained solution at a temperature ≤10 °C. The reaction mixture was allowed to stand for 6 h at 20—25 °C and poured into a cooled 25% aqueous $(NH_4)_2SO_4$ (280 g) with stirring on a magnetic stirrer. The resulting suspension was neutralized to pH = 3—5 with a 25% aqueous ammonia (75 mL). During these manipulations, ice was added to the mixture in order to maintain the temperature below 10 °C. The suspension was allowed to stand for 16 h, a precipitate was filtered off, washed with water (6×20 mL), and dried in air. The filtrate was extracted with AcOEt (3×75 mL) and after standing for a while filtered off through a paper filter. The obtained product and the extract were placed in a flask and stirred with a slight reflux 2 h. Then, the suspension was cooled to room temperature and after 2 h filtered off. A precipitate was washed with AcOEt (2×10 mL) and dried in air to obtain a mixture of three isomers of compound **4** (9.3 g, 93.5%). According to the HPLC data, the content of the main product was 68.4%. The crystallization from nitromethane allowed us to increase the melting point form 270 °C (decomp.) to 303—304 °C (decomp.), as well as to increase the content of the *para*-isomer of compound **4** to 89.0%. The IR and NMR spectra and the results of elemental analysis correspond to those obtained earlier.

Table 1. Retention time (τ) and content (*C*) of components in the products of incomplete nitration of compound **4** by methods ***A*** and ***B***

A		***B***		Product
τ/min	*C* (%)	τ/min	*C* (%)	
3.55	1.60			**10**
5.57	2.90			**4**
6.25	21.09			**4**
6.44	16.34			**4**
6.93	8.20			**9**
7.61	5.04			*m*-NB
7.76	2.26			*p*-NB
7.94	2.26			
9.27	4.96			
9.61	9.43	9.61	10.60	**11**
9.93	6.55			
11.60	5.17			
		11.65	19.40	**12**
		12.16	4.35	
		12.35	2.00	
12.72	1.44			
13.32	1.70	13.32	49.40	**1**

Note. *m*-NB is the *meta*-nitrobenzaldehyde, *p*-NB is the *para*-nitrobenzaldehyde.

2,6,8,12-Tetraacetyl-10-(2,4-dinitrobenzyl)-4-nitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (9). ***A.*** A 99% nitric acid (30 mL) was placed into a three-neck flask equipped with a stirrer and a thermometer, followed by the addition of compound **2** (5.1 g) at −5—0 °C. The reaction mixture was allowed to stand for 1 h at 0 °C and 14 h at room temperature. Then, the mixture was poured into a cooled solution of $(NH_4)_2SO_4$ (112 g) in water (175 mL), the obtained suspension was neutralized to pH = 6—7 with 25% aqueous ammonia (50 mL) (with cooling). A precipitate collected by filtration was washed with water (8×10 mL) and dried in air to obtain the product (6.4 g). According to the HPLC data, the sample contains 0.9% of compound **4**, 50.3% of compound **9**, 11.3% and 1.8% presumably of isomers of compound **9**. For obtaining an analytical sample, the product (0.8 g) was dissolved in MeCN (20 mL) and separated by preparative column chromatography (eluent MeCN).

Most of the isolated fractions contained a mixture of products. Nonetheless, we isolated product (0.25 g) in the individual state with the content of the main compound of 95.2%, which corresponded to 2,6,8,12-tetraacetyl-10-(2,4-dinitrobenzyl)-4-nitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane.

M.p. 250—255 °C. IR, ν/cm^{-1}: 3110, 3043, 2937, 2880, 1671, 1609, 1537, 1396, 1353, 1294, 1131, 1062, 1126, 1040, 945, 887, 852, 836, 808, 776, 725, 663, 596. ^{1}H NMR, δ: 1.96—2.14 (m, 12 H, CH_3CO); 4.12—4.54 (m, 2 H, CH_2); 5.35—5.88 (m, 2 H, CH); 6.47—7.10 (m, 4 H, CH); 7.79 (d, 1 H, Ar, J = 8.4 Hz); 8.50 (d, H, Ar, J = 8.4 Hz); 8.65 (br.s, H, Ar). ^{13}C NMR, δ: 21.03, 22.32 ($\underline{C}H_3CO$); 52.17 (CH_2); 66.8, 69.12, 69.50, 70.85, 71.09, 72.01 (CH); 127.60, 133.15 (CH, Ar); 139.36, 147.52, 149.43 (C, Ar); 167.31, 167.98, 168.67, 168.89 ($CH_3\underline{C}O$).

B. A 99% nitric acid (43 mL) and compound **4** (5.1 g) were placed into a three-neck flask equipped with a stirrer and a thermometer. The reaction mixture was allowed to stand for 14 h at room temperature. Then, the mixture was poured into a cooled 25% aqueous $(NH_4)_2SO_4$ solution (400 g). The obtained suspension was neutralized to pH 5 with 25% aqueous ammonia (95 mL) with cooling by ice, a precipitate was filtered off, washed with water (8×20 mL), and dried in air to obtain the product (6.1 g). The product was treated with AcOEt (70 mL), upon reflux for 1 h, cooled, filtered off, and dried in air. The obtained product (4,85 g) was dissolved in nitromethane (65 mL) (65 mL) with heating, the solution was half concentrated *in vacuo*. After 12 h, the product was collected by filtration, washed with nitromethane (2×5 mL), and dried in air to obtain the product (3.7 g). According to the HPLC data, the sample contained 2% of compound **4**, 78% of compound **9**, 16% and 1.8% presumably of isomers of compound **9**.

Synthesis and isolation of products of incomplete nitration of compound 4. ***A.*** A 99% HNO_3 (30 mL) was placed into a three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser, followed by the addition of NH_4NO_3 (1.2 g) and compound **4** (5.6 g) at a temperature not higher than 25 °C. The reaction mixture was allowed to stand for 30 min without cooling, then heated to 75 °C over 1 h and allowed to stand for 7 h at 75—79 °C. Then, the mixture was cooled and poured into 25% aqueous $(NH_4)_2SO_4$ solution (140 g). The product was collected by filtration, washed with water (8×10 mL), and dried in air. Purification by HPLC gave 2.93 g of the product.

B. The experiments were carried out similarly to ***A***, but the reaction mixture was allowed to stand for 7 h at 95 °C to obtain 2.0 g of the product.

The compositions of obtained products and retention times of components in the HPLC conditions are given in Table 1.

References

1. S. V. Sysolyatin, A. A. Lobanova, Yu. T. Chernikova, G. V. Sakovich, *Russ. Chem. Rev.*, 2005, **8**, 757.
2. A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. More, M. P. Nadler, R.A. Nissan, D. J. Vanderah, *Tetrahedron*, 1998, **54**, 11793.
3. US Pat. 5739325; *Chem. Abstrs*., 1998, **127**, 110983.
4. S. V. Sysolyatin, V. V. Malykhin, *Russ. Chem. Rev.*, 2014, **83**, 949.
5. PCT Int. Appl. WO 9623792; *Chem. Abstrs.*, 1998, **125**, 275920.
6. A. I. Kalashnikov, S. V. Sysolyatin, G. V. Sakovich, I. A. Surmacheva, V. N. Surmachev, Yu. T. Lapina, *Russ. Chem. Bull.* , 2009, **58**, 2164.
7. N. V. Latypow, U. Wellmar, P. Goed, A. J. Bellamy, *Organic Process Research & Development*, 2000, **4**, 156.
8. S. V. Sysolyatin, G. V. Sakovich, A. I. Kalashnikov, Y. T. Chernikova, V. N. Surmachev, A. A. Lobanova, *38st Int. Ann. Conf. of ICT Energetic Materials. Characterisation and Performance of Advanced Systems* (Karlsruhe, FRG, June 27—29, 2007), Fraunhofer ICT, 2007, P 47.
9. G. Jacob, G. Lacroix, V. Destombes, *31st Int. Ann. Conf. of ICT Energetic Materials: Analizys, Diagnostic and Testing* (Karlsruhe, FRG, June 27—30, 2000), Fraunhofer ICT, 2000, P 106.
10. P. Maksimowski, M. Duda, W. Tomaszewski, *Propellants Explos. Pyrotech.*, 2011, **36**, 320.

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