

Chlorination Features of 1,5-Dinitro-3-azabicyclo[3.3.1]non-6-enes

Yu.M. Atroshchenko^a, N.K. Melekhina^a, I.V. Shakhkel'dyan^a, I.E. Yakunina^a,
A.N. Shchukin^a, E.V. Shuvalova^b, and V.A. Subbotin^a

^aL.N.Tolstoi Tula State Pedagogical University, Tula, 300026 Russia

e-mail: reaktiv@tspu.tula.ru

^bZelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow

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Abstract—The electrophilic chlorine addition to 3-substituted 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes in the tetrachloromethane is accompanied at an intramolecular 3,7-cyclization giving 6-chloro-3-R-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chlorides. The reaction of the tricyclic quaternary ammonium salts with sodium methoxide leads to the formation of dealkylated and dehydrohalogenated products, 3-substituted 8-chloro-1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes, bicyclic products with a halogen atom in an allyl position with respect to the double bond.

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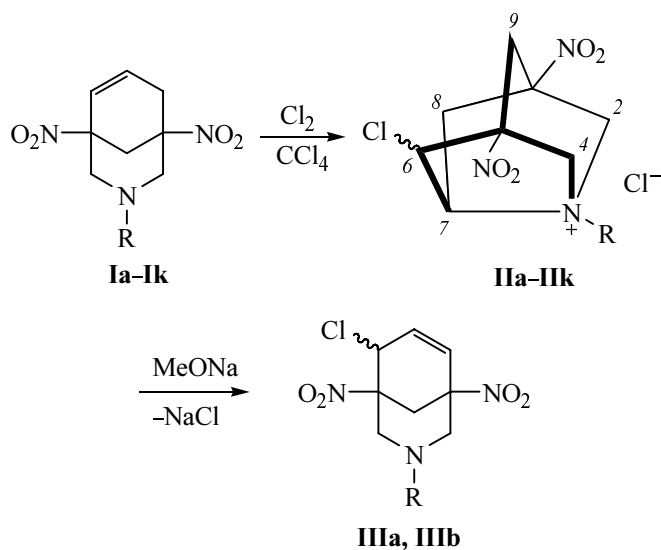
Derivatives of 3-azabicyclo[3.3.1]nonane are known to exhibit a versatile biological activity [1–3]. Therefore the extension of this class compounds is of current importance for it opens new vistas for the purposeful synthesis of biologically active substances and for the study of relations between the structure and properties. One of the ways to functionalization of the previously prepared [4–8] 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes may consist in electrophilic agents addition to the double bond. However the reactivity of the double bond toward

the electrophiles addition is reduced in the 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes because of the presence in the allyl position of the electron-withdrawing 5-NO₂ group. The steric factors characteristic of the cage-like systems also contribute to the double bond deactivation [9]. Therefore we undertook the study of the chlorination of the C=C bond in the cyclohexene fragment of the bicyclic system that had not been investigated before.

We established that at treating the 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **Ia–Ik** with excess chlorine in CCl₄ at room temperature led to the formation instead of the expected products of the halogen addition to the double bond (3-R-6,7-dichloro-1,5-dinitro-3-azabicyclo[3.3.1]nonanes) to their isomers, well soluble in water 3-R-6-chloro-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chlorides **IIa–IIk**. The structure of the compounds as quaternary ammonium salts follows from their IR and NMR spectra and from the elemental analysis.

For instance, the IR spectra of compounds **IIa–IIk** contain strong absorption bands in the region 1550–1600 and 1350–1370 cm⁻¹ corresponding to the stretching vibrations of the nitro groups, and medium bands at 800–850 cm⁻¹ belonging to the C–Cl bands vibrations [10]. The lack in the spectra of the absorption bands from the C=C bond vibrations evidences the saturated character of the compounds synthesized.

The most downfield broadened doublet (δ 5.90–6.10 ppm, ³J 6.0–6.8 Hz) in the ¹H NMR spectra of com-



R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), C₅H₁₁ (**f**), *i*-C₅H₁₁ (**g**), Bn (**h**), (CH₂)₂Br (**i**), (CH₂)₂OH (**j**), (CH₂)₂CO₂H (**k**).

pounds **II** belongs to the proton at the atom C⁶ directly linked to the halogen. The signal from H⁷ proton appears as a broadened triplet (δ 5.10–5.50 ppm, 3J 6.0–6.8 Hz) because of coinciding vicinal coupling constants with the neighboring atoms H⁶ and H⁸. The positive charge on the nitrogen in the tricyclic compounds **II** results in a strong downfield shift ($\Delta\delta \sim 1.0$ ppm) of the signals from the methylene protons H² and H⁴ and from N-alkyl groups (in the α -position) compared to the signals of the corresponding protons in the piperidine ring of the initial compounds **I**, thus confirming the structure of the quaternary ammonium salt. The signals of carbon atoms directly linked to the nitrogen, like those of the protons H² and H⁴, are shifted downfield by 6–7 ppm as compared to the corresponding signals in the ¹³C NMR spectra of substrates **I**. Note that the ¹³C NMR spectra of compounds **II** lack the signals of carbons at the double bond in the region 120–140 ppm confirming the saturated character of the substances. The data obtained are not sufficient for stating the stereochemistry of the C⁶ atom in the molecule of 3-R-6-chloro-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]-nonane chlorides. However the NMR spectra of compounds **II** contain a single set of signals evidencing the presence of an only stereoisomer.

Thus it is presumable that the 6,7-dichloro derivatives primarily formed by chlorine molecule addition to the double bond of bicyclic compounds **I** then transform into a more stable isomeric form, that of tricyclic ammonium salts **II**.

We also found that the treatment of compounds **IIa** and **IIb** with a methanol solution of sodium methoxide at room temperature gave rise to 8-chloro-3-R-1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **IIIa** and **IIIb** (see the scheme). The process involves apparently the dealkylation and the dehydrohalogenation of salts **IIa** and **IIb** under the action of MeONa.

The structure of compounds **IIIa** and **IIIb** was deduced from their NMR spectra. The doublet of doublets from the olefin proton H⁷ appeared in the most downfield part of the spectrum, at δ 6.25–6.26 ppm. The doublets of protons H⁶ and H⁸ were observed in the regions δ 6.15–6.16 and 5.26–5.27 ppm respectively. The diastereotopic protons H², H⁴, and H⁹ gave rise to a group of six well-resolved doublets (2J 10.25–11.25 Hz) in the region δ 2.5–3.4 ppm characteristic of the spectra of unsaturated 1,5-dinitro-substituted 3-azabicyclo[3.3.1]nonanes [4–8]. The signals of carbon atoms at the double bond appear in the ¹³C NMR spectra of the 3-azabicyclic nonenes obtained at δ 126–131 ppm.

Hence our investigations demonstrated the possibility to functionalize the 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes at the C=C bond by means of chlorination and also revealed the specific features of the process consisting in the subsequent intramolecular 3,7-cyclization giving stable tricyclic quaternary salts. The reaction of the latter with the sodium methoxide involved dealkylation and dehydrohalogenation and resulted in the formation of bicyclic compounds with a halogen atom in an allyl position with respect to the double bond.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil or films prepared from acetone solution. NMR spectra were registered on spectrometers Bruker AC-200 and Bruker AC-300 from solutions in DMSO-*d*₆, internal reference HMDS. The melting points were measured on a Boëtius heating block. The purity and homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent acetone–hexane–benzene, 4:1:1 (by volume), spots visualized under UV irradiation.

Initial compounds **Ia–Ik** were prepared by the previously reported procedures [4–8].

6-Chloro-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]-nonane chlorides IIa–IIk. To a solution of 0.44 mmol of 3-substituted 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene **Ia–Ik** in 5 ml of anhydrous CCl₄ was added dropwise a saturated solution of chlorine in CCl₄. The separated colorless precipitate was filtered off, washed with a little CCl₄, and dried in a vacuum desiccator till a constant weight.

3-Methyl-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]-nonane chloride (IIa). Yield 0.131 g (95%), mp 230–231°C (decomp.). ¹H NMR spectrum (200.13 MHz), δ , ppm: 3.06 d (1H, H_a⁸, J 12.7 Hz), 3.20 d (1H, H_e⁹, J 13.19 Hz), 3.31 d.d.d (1H, H_e⁸, J 12.7, 5.86, 1.95 Hz), 3.46 d (1H, H_a⁹, J 13.19 Hz), 3.70 s (3H, NCH₃), 4.43 d.d (1H, H_e⁶, J 11.23, 1.95 Hz), 4.49 d (1H, H_a⁶, J 11.23 Hz), 4.65 d (1H, H_e⁴, J 11.23 Hz), 4.74 d (1H, H_a⁴, J 11.23 Hz), 5.18 t (1H, H⁷, J 6.84 Hz), 6.02 d.d (1H, H⁶, J 6.84, 1.46 Hz). ¹³C NMR spectrum (50.32 MHz), δ , ppm: 30.28 (C⁹), 34.54 (C⁸), 49.69 (NCH₃), 57.47 (C⁶), 66.52 (C⁴), 69.26 (C²), 75.89 (C⁷), 82.88 (C¹), 84.77 (C⁵). Found, %: C 36.11; H 4.21; Cl 23.51; N 14.34. C₉H₁₃Cl₂N₃O₄. Calculated, %: C 36.26; H 4.40; Cl 23.78; N 14.09.

1,5-Dinitro-6-chloro-3-ethyl-3-azoniatricyclo[3.3.1.0^{3,7}]-nonane chloride (IIb). Yield 0.130 g (95%),

mp 242–243°C (decomp.). ¹H NMR spectrum (200.13 MHz), δ, ppm: 1.33 t (3H, NCH₂CH₃, *J* 7.35 Hz), 3.0 d (2H, H_a⁸, *J* 13.2 Hz), 3.10 d (2H, H_c⁸, *J* 13.2 Hz), 3.22 d (1H, H_e⁸, *J* 12.98 Hz), 3.42 d (1H, H_a⁹, *J* 12.98 Hz), 4.03 m (2H, NCH₂CH₃), 4.41 d (2H, H_c⁹, *J* 11.23 Hz), 4.47 d (2H, H_a⁹, *J* 11.23 Hz), 4.57 d (1H, H_e⁹, *J* 10.74 Hz), 4.78 d (1H, H_a⁹, *J* 10.74 Hz), 5.26 t (1H, H⁷, *J* 6.35 Hz), 5.90 d (1H, H⁶, *J* 6.35 Hz). ¹³C NMR spectrum (50.32 MHz), δ, ppm: 8.52 (NCH₂CH₃), 30.73 (C⁹), 34.18 (C⁸), 57.24 (C⁶), 58.0 (NCH₂CH₃), 64.09 (C⁴), 66.24 (C²), 74.98 (C⁷), 82.94 (C¹), 84.77 (C⁵). Found, %: C 38.12; H 4.67; Cl 22.43; N 13.09. C₁₀H₁₅Cl₂N₃O₄. Calculated, %: C 38.48; H 4.84; Cl 22.72; N 13.46.

1,5-Dinitro-3-propyl-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIc). Yield 0.127 g (89%), mp 236–238°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 0.93 t [3H, N(CH₂)₂CH₃, *J* 7.35 Hz], 1.73 m (2H, NCH₂CH₂CH₃), 3.08 d (1H, H_a⁸, *J* 13.24 Hz), 3.18 d (1H, H_c⁸, *J* 13.24 Hz), 3.21 d (1H, H_e⁸, *J* 12.5 Hz), 3.44 d (1H, H_a⁹, *J* 12.5 Hz), 3.98 m (2H, NCH₂CH₂CH₃), 4.48 d (1H, H_c⁹, *J* 10.3 Hz), 4.55 d (1H, H_a⁹, *J* 10.3 Hz), 4.64 d (1H, H_e⁹, *J* 10.3 Hz), 4.86 d (1H, H_a⁹, *J* 10.3 Hz), 5.28 t (1H, H⁷, *J* 7.35 Hz), 5.94 d (1H, H⁶, *J* 7.35 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 10.28 [N(CH₂)₂CH₃], 16.31 (NCH₂CH₂CH₃), 30.6 (C⁹), 34.11 (C⁸), 57.15 (C⁶), 63.37 (NCH₂CH₂CH₃), 64.27 (C⁴), 66.53 (C²), 75.62 (C⁷), 82.95 (C¹), 84.79 (C⁵). Found, %: C 40.22; H 5.48; Cl 21.54; N 13.12. C₁₁H₁₇Cl₂N₃O₄. Calculated, %: C 40.51; H 5.25; Cl 21.74; N 12.88.

3-Isopropyl-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIId). Yield 0.132 g (92%), mp 198–200°C (decomp.). ¹H NMR spectrum (200.13 MHz), δ, ppm: 1.37 d and 1.41 d [3H each, NCH(CH₃)₂], *J* 5.37 Hz), 3.00 d.d (1H, H_a⁸, *J* 13.67, 5.86 Hz), 3.09 d (1H, H_c⁸, *J* 13.67 Hz), 3.23 d (1H, H_e⁸, *J* 12.7 Hz), 3.45 d (1H, H_a⁹, *J* 12.7 Hz), 4.35 m [1H, NCH(CH₃)₂], 4.40 d (1H, H_c⁹, *J* 11.23 Hz), 4.47 d (1H, H_a⁹, *J* 11.23 Hz), 4.52 d (1H, H_e⁹, *J* 11.23 Hz), 4.89 d (1H, H_a⁹, *J* 11.23 Hz), 5.41 t (1H, H⁷, *J* 6.34 Hz), 5.84 d (1H, H⁶, *J* 6.34 Hz). ¹³C NMR spectrum (50.32 MHz), δ, ppm: 16.44 [NCH(CH₃)₂], 31.38 (C⁹), 34.03 (C⁸), 57.15 (C⁶), 62.80 [NCH(CH₃)₂], 62.89 (C⁴), 64.81 (C²), 73.37 (C⁷), 83.02 (C¹), 84.79 (C⁵). Found, %: C 40.57; H 5.46; Cl 21.32; N 12.21. C₁₁H₁₇Cl₂N₃O₄. Calculated, %: C 40.51; H 5.25; Cl 21.74; N 12.88.

3-Butyl-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIe). Yield 0.120 g

(80%), mp 236–237°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 0.95 t [3H, N(CH₂)₃CH₃, *J* 7.36 Hz], 1.33 m [2H, N(CH₂)₂CH₂CH₃], 1.69 m (2H, NCH₂CH₂CH₂CH₃), 3.08 d (1H, H_a⁸, *J* 12.5 Hz), 3.19 d (1H, H_c⁸, *J* 12.5 Hz), 3.22 d (1H, H_e⁸, *J* 12.5 Hz), 3.44 d (1H, H_a⁹, *J* 12.5 Hz), 4.0 m [2H, NCH₂(CH₂)₂CH₃], 4.46 d (1H, H_c⁹, *J* 10.3 Hz), 4.55 d (1H, H_a⁹, *J* 10.3 Hz), 4.62 d (1H, H_e⁹, *J* 10.29 Hz), 4.85 d (1H, H_a⁹, *J* 10.29 Hz), 5.27 t (1H, H⁷, *J* 6.62 Hz), 5.95 d (1H, H⁶, *J* 6.62 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 13.28 [N(CH₂)₃CH₃], 18.97 [N(CH₂)₂CH₂CH₃], 24.39 (NCH₂CH₂CH₂CH₃), 30.6 (C⁹), 34.09 (C⁸), 57.13 (C⁶), 61.92 [NCH₂(CH₂)₂CH₃], 64.24 (C⁴), 66.49 (C²), 75.61 (C⁷), 82.92 (C¹), 84.76 (C⁵). Found, %: C 42.22; H 5.24; Cl 20.41; N 12.12. C₁₂H₁₉Cl₂N₃O₄. Calculated, %: C 42.37; H 5.63; Cl 20.84; N 12.35.

1,5-Dinitro-3-pentyl-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIIf). Yield 0.134 g (86%), mp 231–233°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 0.90 t [(3H, N(CH₂)₄CH₃, *J* 7.35 Hz], 1.31 m [4H, N(CH₂)₂CH₂CH₂CH₃], 1.73 m [2H, NCH₂CH₂(CH₂)₂CH₃], 3.06 d (1H, H_a⁸, *J* 13.19 Hz), 3.21 d (1H, H_c⁸, *J* 12.21 Hz), 3.28 d.d (1H, H_e⁸, *J* 13.19, 1.96 Hz), 3.45 d (1H, H_a⁹, *J* 12.21 Hz), 4.03 m [2H, NCH₂(CH₂)₃CH₃], 4.48 d (1H, H_c⁹, *J* 10.25 Hz), 4.65 d (1H, H_a⁹, *J* 11.48 Hz), 4.58 d (1H, H_e⁹, *J* 10.25 Hz), 4.90 d (1H, H_a⁹, *J* 11.48 Hz), 5.27 t (1H, H⁷, *J* 6.83 Hz), 5.99 d (1H, H⁶, *J* 6.83 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 13.55 [N(CH₂)₄CH₃], 21.42 [N(CH₂)₃CH₂CH₃], 22.13 [N(CH₂)₂CH₂CH₂CH₃], 27.60 [NCH₂CH₂(CH₂)₂CH₃], 30.53 (C⁹), 34.03 (C⁸), 57.12 (C⁶), 61.98 [NCH₂(CH₂)₃CH₃], 64.09 (C⁴), 66.32 (C²), 75.57 (C⁷), 82.91 (C¹), 84.74 (C⁵). Found, %: C 44.23; H 5.91; Cl 20.73; N 12.04. C₁₃H₂₁Cl₂N₃O₄. Calculated, %: C 44.08; H 5.98; Cl 20.02; N 11.86.

3-Isopentyl-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIg). Yield 0.134 g (86%), mp 231–233°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 0.96 d [6H, N(CH₂)₂CH(CH₃)₂, *J* 5.86 Hz], 1.62 m [3H, NCH₂CH₂CH(CH₃)₂], 3.07 d (1H, H_a⁸, *J* 13.18 Hz), 3.22 d (1H, H_c⁸, *J* 12.7 Hz), 3.19 d.d (1H, H_e⁸, *J* 13.18, 1.96 Hz), 3.43 d.t (1H, H_a⁹, *J* 12.7, 1.96 Hz), 4.04 m [2H, NCH₂CH₂CH(CH₃)₂], 4.45 d (1H, H_c⁹, *J* 10.26 Hz), 4.52 d (1H, H_a⁹, *J* 10.26 Hz), 4.62 d (1H, H_e⁹, *J* 10.75 Hz), 4.83 d (1H, H_a⁹, *J* 10.75 Hz), 5.27 t (1H, H⁷, *J* 6.84 Hz), 5.96 d.d (1H, H⁶, *J* 6.84, 1.46 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 22.02 [N(CH₂)₂CH(CH₃)₂], 25.62 [N(CH₂)₂CH(CH₃)₂], 30.59 [NCH₂CH₂CH(CH₃)₂], 30.70 (C⁹), 34.06 (C⁸), 57.12 (C⁶),

61.11 [NCH₂CH₂CH(CH₃)₂], 64.23 (C⁴), 66.46 (C²), 75.66 (C⁷), 82.94 (C¹), 84.77 (C⁵). Found, %: C 44.34; H 5.94; Cl 19.76; N 12.21. C₁₃H₂₁Cl₂N₃O₄. Calculated, %: C 44.08; H 5.98; Cl 20.02; N 11.86.

3-Benzyl-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIh). Yield 0.151 g (92%), mp 217–218°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 3.16 d (1H, H_a⁸, *J* 12.5 Hz), 3.24 d (1H, H_e⁶, *J* 12.5 Hz), 3.32 d.d (1H, H_e⁸, *J* 12.5, 4.42 Hz), 3.38 d (1H, H_a⁹, *J* 12.5 Hz), 3.80 d (1H, H_e⁹, *J* 10.3 Hz), 4.18 d (1H, H_e⁴, *J* 10.3 Hz), 4.83 d (1H, H_a⁹, *J* 10.3 Hz), 5.06 d (1H, H_a⁴, *J* 10.3 Hz), 5.47 m (1H, H⁷), 5.28 d and 5.48 d (1H each, NCH₂Ph, *J* 12.0 Hz), 6.11 d (1H, H⁶, *J* 7.36 Hz), 7.55 m (3H, H_{arom}), 7.75 m (2H, H_{arom}). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 30.43 (C⁹), 34.38 (C⁸), 57.21 (C⁶), 63.94 (NCH₂Ph), 64.45 (C⁴), 66.52 (C²), 75.58 (C⁷), 82.73 (C¹), 84.76 (C⁵), 127.68, 129.27, 130.66, 131.84 (C_{arom}). Found, %: C 47.88; H 4.32; Cl 18.62; N 11.36. C₁₅H₁₇Cl₂N₃O₄. Calculated, %: C 48.14; H 4.58; Cl 18.95; N 11.23.

3-(2-Bromoethyl)-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIi). Yield 0.168 g (98%), mp 195–196°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 3.05 d (2H, H_a⁸, *J* 12.5 Hz), 3.21 d.d (2H, H_e⁸, *J* 12.5, 5.86 Hz), 3.23 d (1H, H_e⁹, *J* 12.5 Hz), 3.42 d (1H, H_a⁹, *J* 12.5 Hz), 3.95 t and 4.19 t (1H each, NCH₂CH₂Br, *J* 6.62 Hz), 4.42 d (1H, H_e⁹, *J* 10.3 Hz), 4.45 m and 4.72 m (1H each, NCH₂CH₂Br), 4.50 d (1H, H_a⁹, *J* 10.3 Hz), 4.69 d (1H, H_e⁴, *J* 10.3 Hz), 4.77 d (1H, H_a⁴, *J* 10.3 Hz), 5.42 m (1H, H⁷), 5.85 d (1H, H⁶, *J* 6.35 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 30.44 (C⁹), 34.04 (C⁸), 36.70 (NCH₂CH₂Br), 56.97 (C⁶), 62.15 (NCH₂CH₂Br), 65.18 (C⁴), 67.44 (C²), 77.09 (C⁷), 82.90 (C¹), 84.65 (C⁵). Found, %: C 30.54; H 3.32; N 10.45. C₁₀H₁₄BrCl₂N₃O₄. Calculated, %: C 30.71; H 3.61; N 10.75.

3-(2-Hydroxyethyl)-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIj). Yield 0.123 g (85%), mp 241–243°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 3.07 d (2H, H_a⁸, *J* 12.7 Hz), 3.22 d (1H, H_e⁸, *J* 12.94 Hz), 3.24 d.d (2H, H_e⁸, *J* 12.7, 1.95 Hz), 3.45 d.t (1H, H_a⁹, *J* 12.94, 1.95 Hz), 3.90 t (2H, NCH₂CH₂OH, *J* 4.89 Hz), 4.12 m (2H, NCH₂CH₂OH), 4.47 d.d (1H, H_e⁹, *J* 10.75, 1.95 Hz), 4.54 d (1H, H_a⁹, *J* 10.5 Hz), 4.66 d (1H, H_e⁴, *J* 11.23 Hz), 4.80 d (1H, H_a⁴, *J* 11.23 Hz), 5.34 t (1H, H⁷, *J* 6.84 Hz), 5.93 d.d (1H, H⁶, *J* 6.84, 0.98 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 30.62 (C⁹), 34.06 (C⁸), 55.18 (NCH₂CH₂OH), 57.20 (C⁶), 64.09 (NCH₂CH₂OH),

65.60 (C⁴), 67.73 (C²), 76.55 (C⁷), 82.88 (C¹), 84.61 (C⁵). Found, %: C 36.33; H 4.24; Cl 21.21; N 12.45. C₁₀H₁₅Cl₂N₃O₅. Calculated, %: C 36.60; H 4.61; Cl 21.61; N 12.81.

3-(2-Carboxyethyl)-1,5-dinitro-6-chloro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane chloride (IIk). Yield 0.146 g (97%), mp 201–201°C (decomp.). ¹H NMR spectrum (300.13 MHz), δ, ppm: 3.04 d (2H, H_a⁸, *J* 13.2 Hz), 3.18 d.d (2H, H_e⁸, *J* 13.2, 1.95 Hz), 3.21 d (1H, H_e⁹, *J* 12.5 Hz), 3.38 m (2H, NCH₂CH₂CO₂H), 3.40 d (1H, H_a⁹, *J* 12.5 Hz), 4.16 t (2H, NCH₂CH₂CO₂H, *J* 6.84 Hz), 4.44 d (1H, H_e⁹, *J* 10.25 Hz), 4.48 d (1H, H_a⁹, *J* 10.25 Hz), 4.57 d (1H, H_e⁴, *J* 11.23 Hz), 4.80 d (1H, H_a⁴, *J* 11.23 Hz), 5.37 t (1H, H⁷, *J* 5.86 Hz), 5.87 d (1H, H⁶, *J* 5.86 Hz), 12.0 br.s [N(CH₂)₂CO₂H]. ¹³C NMR spectrum (75.47 MHz), δ, ppm: 30.53 (C⁹), 30.70 (NCH₂CH₂CO₂H), 34.05 (C⁸), 57.04 and 57.44 (C⁶), 60.74 (NCH₂CH₂CO₂H), 64.70 (C⁴), 66.97 (C²), 75.99 (C⁷), 82.82 (C¹), 84.60 (C⁵), 169.02 [N(CH₂)₂CO₂H]. Found, %: C 37.15; H 4.19; Cl 20.01; N 11.88. C₁₁H₁₅Cl₂N₃O₆. Calculated, %: C 37.10; H 4.25; Cl 19.91; N 11.80.

1,5-Dinitro-8-chloro-3-azabicyclo[3.3.1]non-6-enes IIIa and IIIb. To a solution of 0.4 mmol of compounds IIa and IIb in 5 ml of anhydrous MeOH was added a solution of sodium methoxide obtained by dissolving 4 mmol of Na in 5 ml of MeOH. The reaction mixture was stirred at 20°C till the initial chloride dissolved completely. The solvent was evaporated by half, the residue was cautiously treated with water, and the reaction products separated as colorless crystalline precipitates. The latter were recrystallized from ethanol with addition of an activated carbon.

3-Methyl-1,5-dinitro-8-chloro-3-azabicyclo[3.3.1]non-6-ene (IIIa). Yield 0.093 g (89%), mp 124–125°C. ¹H NMR spectrum (300.13 MHz), δ, ppm: 2.30 s (3H, NCH₃), 2.54 d (1H, H_a⁸, *J* 10.4 Hz), 2.59 d (1H, H_a⁴, *J* 10.26 Hz), 2.74 d (1H, H_a⁹, *J* 11.23 Hz), 2.83 d (1H, H_e⁹, *J* 11.23 Hz), 2.97 d (1H, H_e⁸, *J* 10.4 Hz), 3.43 d (1H, H_e⁴, *J* 10.26 Hz), 5.27 d (1H, H⁸, *J* 4.4 Hz), 6.16 d (1H, H⁶, *J* 9.28 Hz), 6.26 d.d (1H, H⁷, *J* 9.28, 4.4 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 31.66 (C⁹), 43.55 (NCH₃), 56.88 (C⁸), 56.96 (C⁴), 59.96 (C²), 86.74 (C¹), 87.79 (C⁵), 126.46 (C⁷), 130.32 (C⁶). Found, %: C 41.27; H 4.59; Cl 13.61; N 15.95. C₉H₁₂ClN₃O₄. Calculated, %: C 41.31; H 4.62; Cl 13.55; N 16.06.

1,5-Dinitro-8-chloro-3-ethyl-3-azabicyclo[3.3.1]non-6-ene (IIIb). Yield 0.075 g (68%), mp 85–86°C. ¹H NMR spectrum (300.13 MHz), δ, ppm: 0.96 t

(3H, NCH₂CH₃), 2.54 q (2H, NCH₂CH₃, *J* 7.08 Hz), 2.60 d (1H, H_a², *J* 10.25 Hz), 2.67 d (1H, H_a⁴, *J* 10.5 Hz), 2.77 d (1H, H_a⁹, *J* 11.25 Hz), 2.81 d (1H, H_e⁶, *J* 11.25 Hz), 3.00 d (1H, H_e⁵, *J* 10.25 Hz), 3.44 d (1H, H_e⁴, *J* 10.5 Hz), 5.26 d (H, H⁸, *J* 3.91 Hz), 6.15 d (1H, H⁶, *J* 9.76 Hz), 6.25 d.d (1H, H⁷, *J* 9.76, 3.91 Hz). ¹³C NMR spectrum (75.47 MHz), δ, ppm: 11.08 (NCH₂CH₃), 32.11 (C⁹), 49.55 (NCH₂CH₃), 54.65 (C⁸), 56.98 (C⁴), 57.8 (C²), 86.88 (C¹), 87.85 (C⁵), 126.35 (C⁷), 130.38 (C⁶). Found, %: C 43.56; H 5.03; Cl 12.87; N 15.42. C₁₀H₁₄ClN₃O₄. Calculated, %: C 43.57; H 5.12; Cl 12.86; N 15.24.

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