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3-Azabicyclo[3.3.1]nonane Derivatives: VIII.* Synthesis and Properties of 6(7)-R-3,3-Dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene Iodides

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Abstract—*N*-Alkylation of 6(7)-R-1,5-dinitro-3-methyl-3-azabicyclo[3.3.1]non-6-enes with methyl iodide afforded a series of quaternary ammonium salts whose yield depended on the solvent polarity and character of substituents located in positions 6 or 7 of substrate. The presence of electron-withdrawing groups reduced the yield of the target products compared to unsubstituted compound, whereas the electron-donor substituents increased the yield. As shown by the X-ray diffraction study the congormation of the substances was not changed in the course of quaternization. The DTA-TG analysis revealed that in the first stage of thermolysis the 6(7)-R-3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodides suffer dealkylation. Two fragmentation paths of compounds synthesized under electron impact were observed: elimination either of methyl iodide or aziridinium cation.

In extension of research [1–5] on the synthesis of polyfunctional 3-azabicyclo[3.3.1]nonanes, a valuable class of biologically active substances [6], in the present study we investigated alkylation of 1,5-dinitro-3-methyl-3-azabicyclo[3.3.1]non-6-ene derivatives with alkyl iodides. The interest of this reaction lies in the change in the hydrophilic/lipophilic characteristics of compounds on going from neutral nitrogen-containing heterocycles to their quaternary salts. These properties are important for bonding with enzymes and receptors, for transport through membranes, penetration into cells, and distribution in tissues

As substrates in the study of 3-azabicyclononanes alkylation were selected 6(7)-R-3-methyl-1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **I** prepared from derivatives of 1,3-dinitrobenzene along Scheme 1 [2–4, 7, 8], and methyl iodide was used as alkylation agent. The reaction in acetonitrile at 60°C completed within 48 h. The replacement the solvent by less polar tetrahydrofuran resulted in decreased a yield of alkylation products. These reactions furnished compounds **IIa–i** whose composition and structure are confirmed by elemental analyses and spectral data. The yield of quaternary salts is significantly affected with the nature of substituents located in positions *6* or *7* of substrate **I**. . The presence of electron-withdrawing groups reduced the yield of the target products compared to unsubstituted compound, whereas the electron-donor substituents increased the yield. We failed to obtain alkylation products from 3-azabicyclo-[3.3.1]-nonane derivatives containing other substituents at the nitrogen atom, like Et, EtBr, CH_2Ph, CH_2CO_2H, EtOH, $CH(C_2H_5)OH$. These data indicate that more bulky groups provide steric hindrances to the attack of the nitrogen by methyl iodide. This conclusion is indirectly supported by the fact that the attempt to carry out the alkylation with ethyl iodide failed even with N-methyl derivatives of 3-azabicyclononane.

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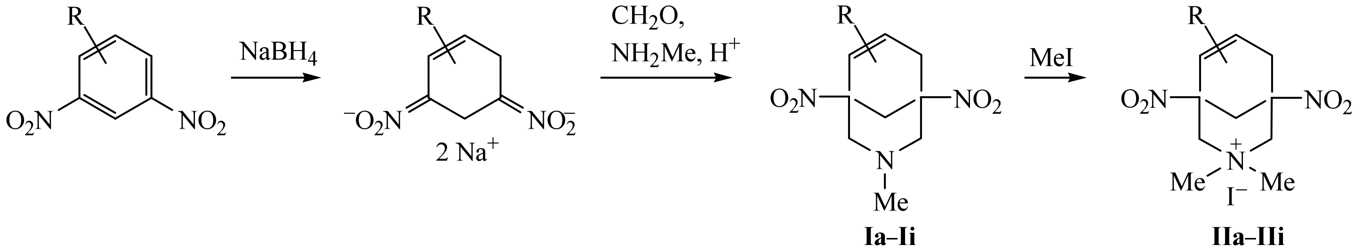
* For Communication VII see [1].

Scheme 1.



R = H (**a**), 6-Me (**b**), 6-OMe (**c**), 6-O$(CH_2)_2$Cl (**d**), 6-OPh (**e**), 6-Cl (**f**), 6-Br (**g**), 7-OMe (**h**), 7-$CONH_2$ (**i**).

In the IR spectra of compounds synthesized the most characteristic absorption bands are those of stretching vibrations of C=C bonds and NO_2 groups in the region 1630–1675, 1540–1570, and 1340–1375 cm^{-1}. The absorption bands in the IR spectra of quaternary salts **II** are shifted to higher frequencies as compared to those of the initial 3-azabicyclo[3.3.1]-non-6-enes **I** due to the presence in the former of a positive charge on the nitrogen atom.

The assignment of signals in the ^1H NMR spectra can be illustrated by an example of iodide **IIe** (Fig. 1). The most downfield signals at δ 7.10–7.50 ppm are a doublet and two triplets (^3J 7.93 Hz) with integral intensity ratio 2 : 2 : 1 corresponding to aromatic protons from the OPh group. The signal of olefin proton H^7 gives an *ABX* system with protons H^8 and is observed as a doublet of doublets (^3J 4.89 and 2.80 Hz) at δ 5.50 ppm. Therewith the signals of the *AB* part contains a broadened doublet

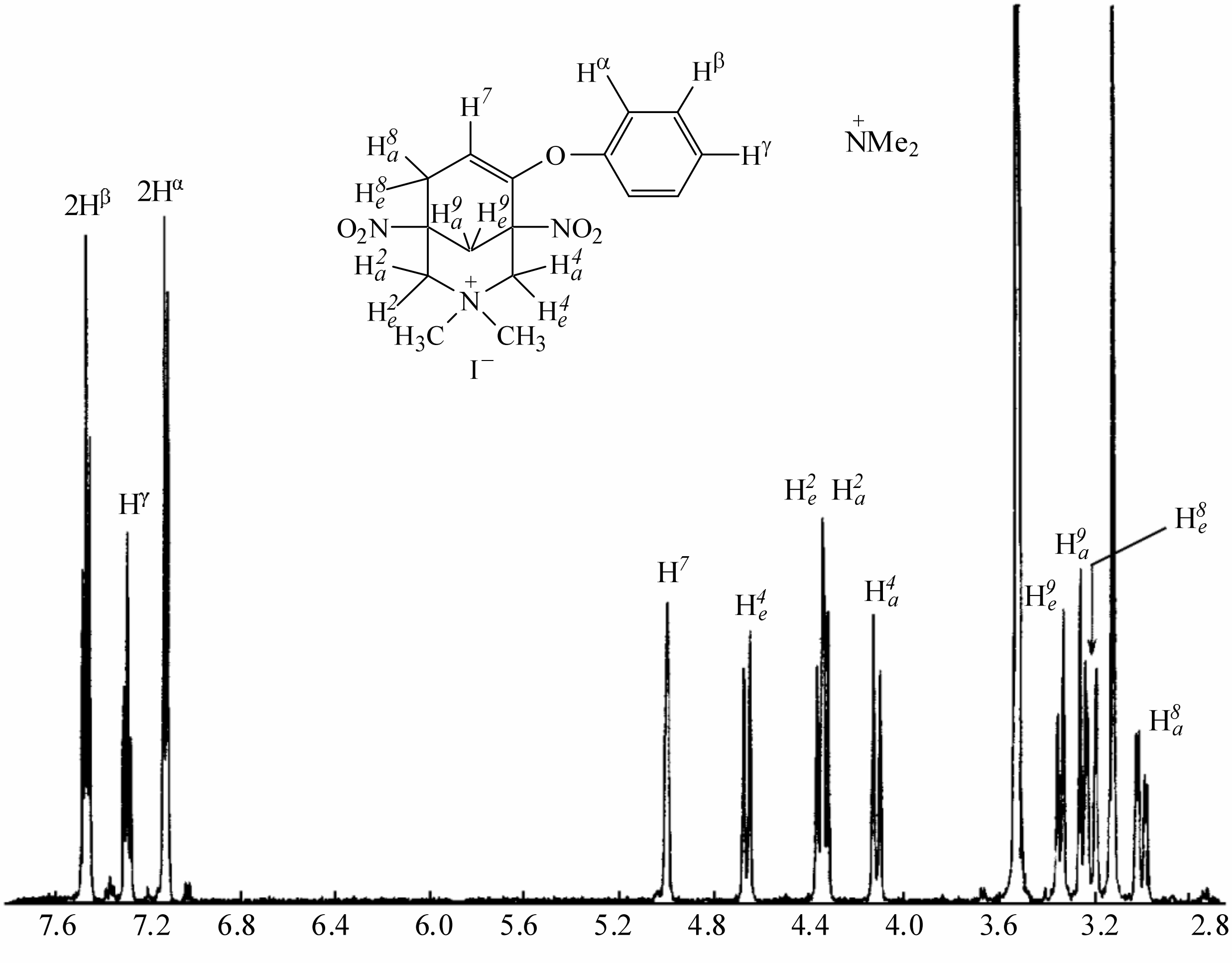


Fig. 1. ^1H NMR spectrum of 6-phenoxy-3,3-dimethyl-1,5-dinitro-3-azoniabicyclo-[3.3.1]non-6-ene iodide **IIe.**

(^2J 18.31 Hz) of H^8_e proton and a well resolved doublet of doublets (^2J 18.31, ^3J 4.89 Hz) of H^8_a proton at δ 3.21 and 2.30 ppm respectively. The signals of bridging protons H^9 appear as two doublets (^2J 11.60 Hz) at δ 3.34 and 3.25 ppm The positive charge on the nitrogen of the piperidine ring causes a strong downfield shift (Δδ ~1.0 ppm) of methylene protons $H^{2,4}$ signals (δ 4.11–4.66 ppm) and those of nonequivalent N-methyl groups (δ 3.52, 3.53 ppm) as compared to the signals of the corresponding protons in the initial compound **Ie** (δ 2.47–3.53 and 2.53 ppm respectively) (see EXPERIMENTAL).

Similar values of the geminal coupling constants of the protons in the piperidine ring in the ^1H NMR spectra of quaternary salts **II** and the initial 3-azabicyclo[3.3.1]-non-6-enes **I** evidence that the spatial structure of the bicyclononenes does not considerably change during quaternization. It was formerly established with the use of X-ray diffraction analysis [2–4, 9] that in the series of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene derivatives the piperidine ring exists in the *chair* form, and the cyclohexane ring has *sofa* conformation. Yet the X-ray data on 7,7-dimethyl-3-thia-7-azoniabicyclo[3.3.1]-nonan-9-one iodide [10] revealed that the ring containing the NMe_2^+ group was in a *boat* form. It was therefore expectable that on alkylation of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **I** the nitrogen-containing fragment would acquire a *boat* form. To clear up this problem we subjected one of the compounds synthesized, 3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide **IIa**, to X-ray diffraction analysis.

As show the data obtained (Tables 1, 2, Fig. 2) the cation of quaternary salt **IIa** retained the conformation of the initial compound. The piperidine ring in the compound under study has the *chair* form. Deviations of atoms N^3 and C^9 from the plane going through the rest ring atoms amount to 0.512 and –0.799 Å respectively. The conformation of cyclohexene ring $C^1C^8C^7C^6C^5C^9$ is *sofa* with a deviation of C^9 atom from the plane of the other ring atoms of –0.776 Å. The conformation of the eight-membered ring is close to *boat-boat* one and its Zefirov–Palyulin folding parameters [11] are as follows: S_2 1.186, S_3 0.382, S_4 0.683, φ_2 182.93, φ_3 180.66. The nitro groups attached to atoms C^1 and C^5 take an equatorial positions [torsion angles $N^1C^1C^9C^5$ and $N^2C^5C^9C^1$ are equal to 179.6(3) and –179.1(3) deg respectively]. They are also considerably turned with respect to relatively planar fragment of the cyclohexene ring [torsion angles $O^2N^1C^1C^8$ and $O^3N^2C^5C^6$ are equal to 44.9(5) and 93.4(4) deg respectively].

The bonds C–N^+ in cation **IIa** are somewhat longer that usual bonds of this type (1.499 Å [12]) indicating that in cation **IIa** exist steric hindrances. This is confirmed by the presence in this fragment of cation of quite a number of shortened interatomic contacts: $C^7\cdots C^{11}$ 3.30 (3.42 Å, here and hereinafter in parentheses is given the sum of vander Waals radii [13] of the corresponding atoms), $C^8\cdots C^{11}$ 3.24, $C^7\cdots H^{11C}$ 2.68 (2.87), $C^8\cdots H^{11C}$ 2.77, $H^{2B}\cdots H^{11B}$ 2.21 (2.32), $H^{4B}\cdots H^{10B}$ 2.02 Å. Eight hydrogen atoms are present in the nearest coordination sphere of the iodide ion forming shortened contacts I···H that are closer than the sum of van der Waals radii of C and H atoms (3.30 Å [13]): $I^1\cdots H^{2B}$ 2.92, $I^1\cdots H^{11B}$ 3.12, $I^1\cdots H^{6B2}$ $(1 + x, 1 + y, z)$ 3.24, $I^1\cdots H^{4A2}$ 3.00, $I^1\cdots H^{4B2\ 2}$ $(1 - x, 0.5 + y, 1 - z)$ 3.09, $I^1\cdots H^{9B2\ 2}$ 2.94, $I^1\cdots H^{10B2\ 2}$ 3.13, $I^1\cdots H^{9A2\ 2\ 2}$ $(1 + x, y, 1 + z)$ 2.91 Å. It is interesting that all these contacts save $I^1\cdots H^{6B2}$ 3.24 Å are also shorter than the so-called statistical mean value (3.13 Å) established recently for I···H contact [14].

Sterical "overloading" of the molecules of compounds synthesized is reflected in the pattern of their

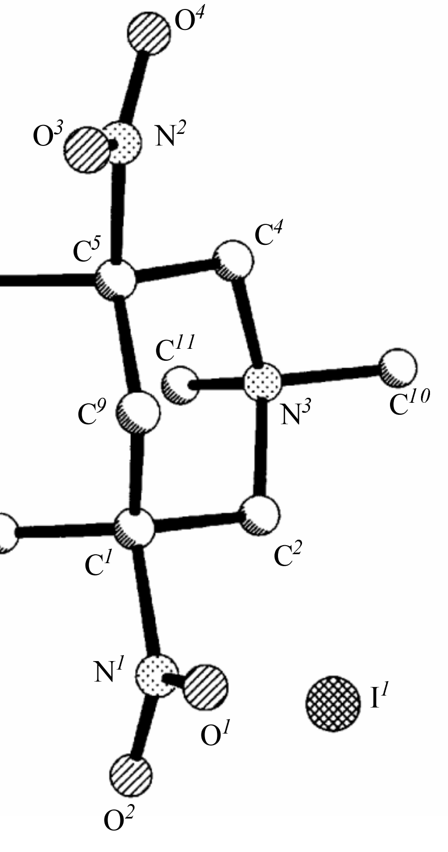


Fig. 2. Molecular structure of 3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide **IIa**.

Table 1. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($E^2 \times 10^3$) of nonhydrogen atoms in the structure of 3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide **IIa**

Atom	*x*	*y*	*z*	U_{eq}
I^1	8337(1)	4576(1)	6926(1)	17(1)
N^1	–2228(4)	2506(3)	2013(4)	18(1)
N^2	3190(4)	3651(3)	973(4)	21(1)
N^3	2745(4)	3299(3)	5167(4)	14(1)
O^1	–2993(4)	2191(3)	514(4)	29(1)
O^2	–2784(4)	2278(3)	3096(4)	26(1)
O^3	2754(5)	2770(4)	–29(5)	35(1)
O^4	4435(4)	4401(4)	1182(4)	32(1)
C^1	–454(5)	3298(3)	2603(4)	13(1)
C^2	767(4)	2838(3)	4439(4)	17(1)
C^4	3536(5)	3308(4)	3844(5)	16(1)
C^5	2150(6)	3833(4)	2084(5)	17(1)
C^6	1722(6)	5230(5)	2061(6)	21(1)
C^7	143(6)	5542(4)	2209(5)	25(1)
C^8	–1096(4)	4656(7)	2448(4)	19(1)
C^9	429(5)	3040(3)	1390(4)	15(1)
C^{10}	2986(4)	4547(6)	6071(4)	19(1)
C^{11}	3914(5)	2382(3)	6552(4)	19(1)

Table 2. Some bond lengths (*d*, Å) in the structure of 3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide **IIa**.

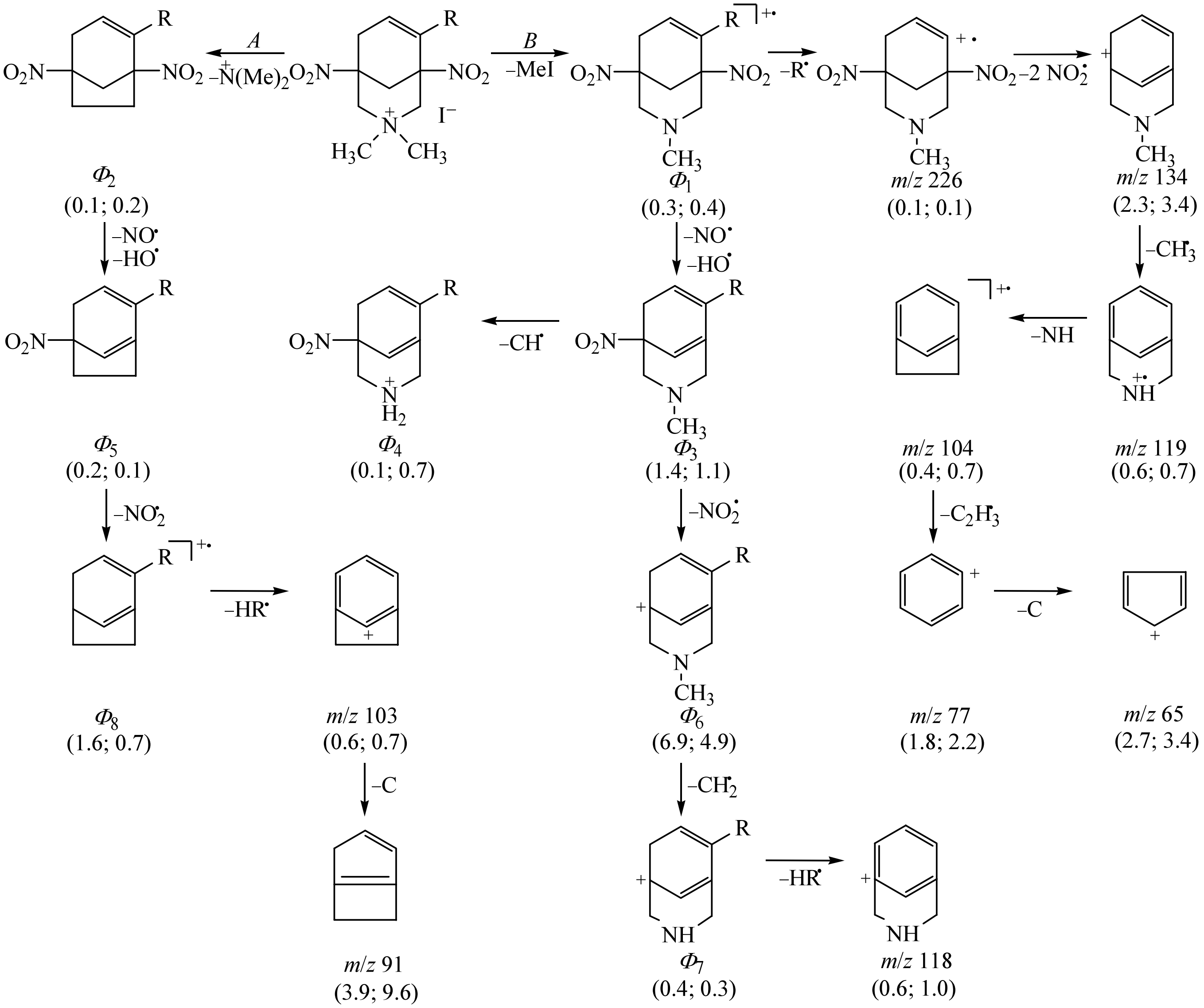
Bond	*d*, Å	Bond	*d*, Å
O^1–N^1	1.222(5)	N^3–C^{11}	1.514(6)
O^2–N^2	1.234(5)	C^1–C^2	1.548(6)
O^3–N^2	1.215(4)	C^1–C^9	1.508(5)
O^4–N^2	1.225(4)	C^1–C^8	1.529(5)
N^1–C^1	1.535(5)	C^7–C^8	1.373(6)
N^2–C^5	1.544(4)	C^6–C^7	1.452(7)
N^3–C^2	1.531(4)	C^5–C^6	1.526(8)
N^3–C^4	1.518(4)	C^5–C^9	1.525(5)
N^3–C^{10}	1.516(4)	C^4–C^5	1.539(5)

decomposition under electron impact as revealed in analysis of the mass spectra of compounds **IIf, g** (Scheme 2; relative intensities of ion peaks with respect to the total ion current are given in parentheses). It was shown formerly [1, 4] that the main fragmentation path for molecular ion of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **I** was the rapture of C–N bond with radicals NO_2 elimination which in some cases involved nitro-nitrite rearrangement often observed in nitro compounds [15]. In contrast to initial compounds **I** for salts **IIf, g** a primary dissociation of the C–N bonds in the heterocyclic fragment is characteristic in keeping with the X-ray analysis data and in agreement with the properties of amines quaternary salts [16]. Along one of the fragmentation paths of molecular ions an elimination of dimethylaminocation Me_2N^+ (*m/z* 44) occurs (path *A*). The cation further loses a hydrogen molecule converting into an aziridinylium cation of *m/z* 42 with a very high relative peak intensity (maximum in the case of compound **IIf**). Further fragmentation of the Φ_2 ion results in bicyclodiene (*m/z* 91) (Scheme 2).

Another fragmentation path (path *B*) consists in elimination of methyl iodide and formation of ion Φ_1. Interestingly, the positive charge can be localized either on the eliminated species or on the remaining fragment. The prevailing direction is formation of a cation-radical $MeI^{+\cdot}$ (*m/z* 142) whose peak in the mass spectrum of compound **IIg** is the strongest. In the course of cation Φ_1 fragmentation it loses in succession radical species $NO^\cdot$, $OH^\cdot$, and $NO_2^\cdot$. Another path of cation Φ_1 fragmentation starts with halogen atoms elimination (Scheme 2).

The study of the thermal stability of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene derivatives [1] showed that they were prone to decomposition with elimination of one or two nitro groups in agreement with the properties of aliphatic nitro compounds [17]. Therefore we studied the behavior of compounds **IIa–i** at heating by means of derivatography. The thermogravimetric data (DTG and TG) reveled that for all compounds under study two pronounced stages of mass loss are observed: the first one with an endo effect, the second one with exo effect (Table 3). From analysis of signals on DTA thermograms ehthalpy (*Q*), apparent activation energy (E_a), and orders (*n*) of the thermal degradation of compounds **IIa–i** were calculated. The comparison of calculated and experimental values of mass loss (Δm) suggests that in the first stage of thermolysis (115–220°C) dealkylation occurs with methyl iodide elimination and formation of the corresponding derivatives of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene **I.** The process occurs with heat consumption and with relatively high activation energy (101–163 kJ mol^{-1}) evidencing the high stability of the quaternary salts. The second stage (218–310°C) for the most compounds proceeds with notable heat liberation (163–361 kJ mol^{-1}) and with low activation energy (40–110 kJ mol^{-1}). Compounds with alkoxy groups in positions *6* or *7* **IIc, d, h** form an exception with an enthalpy in the limits 71–94 kJ mol^{-1}.

Scheme 2.



EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75-IR from films prepared from acetone solution or from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometer Bruker DRX-500 (500 MHz) in DMSO-d_6, internal references HMDS. Mass spectra of compounds were taken on Varian MAT-311 instrument at ionizing electrons energy 70 eV. Combined measurements of DTA, DTG, and TG were carried out on derivatogrph Q-1500 (MOM, Hungary) in a labyrinth crucible in air under dynamic conditions [18], heating rate 1.25 deg min^{-1} in the temperature range 20–500°C. Alumina calcined at 1200°C was used as inert carrier. Weight of the samples studied was 100 mg. The sensitivity to mass loss in TG was 0.2 mg, the sensitivity in recording DTG and DTA was 50 and 500 μV respectively. The temperature of the start and the end of decomposition was determined at the points were DTG and DTA curves crossed the basis lines. The maximum temperature of decomposition process corresponded to the extremum on the DTA curve. The enthalpy was estimated from the DTA curves by procedure [19].

Initial compounds **Ia–c, f, h, i** were prepared by procedures from [2, 7, 8]. Compounds **Id, e, g** were synthesized in a similar way.

Table 3. Evaluation of thermal stability of 6(7)-R-3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodides **IIa–i**

Compd. no.	Stage I								Stage II					
	start, °C	maximum, °C	end °C	Δ*m*, calc., %	Δ*m*, exp, %	*Q*, kJ/mol	E_a, kJ/mol	reaction order, *n*	start, °C	maximum, °C	end, ° C	Δ*m* calc., %	*Q*, kJ/mol	E_a, kJ/mol
IIa[a]	158	185	204	39	41	–98	114	2.5	219	257	268	75	302	66
IIb	175	190	203	37	46	–127	121	2.8	219	263	285	90	163	105
IIc[a]	155	174	198	36	34	–132	101	1.3	232	285	302	86	83	45
IId	157	167	193	31	29	–264	138	2.2	240	250	277	61	71	110
IIe[a]	163	169	200	31	29	–124	156	2.9	254	293	310	71	362	50
IIf	165	173	200	35	37	–106	103	2.2	218	262	286	86	263	49
IIg	175	181	200	32	29	–107	102	2.2	230	253	273	60	264	40
IIh	173	193	220	36	32	–96	146	2.5	238	288	316	82	94	70
IIi	193	203	220	35	34	–196	163	1.3	220	240	262	53	200	45

[a] Sublimation of compound is observed.

6-(2-Chloroethoxy)-3-methyl-1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene (Id). Yield 27%. Colorless crystals, mp 83–84°C. IR spectrum, cm^{-1}: 1669 (C=C), 1527, 1333 (NO_2), 1226 (C–O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.01 d.d (1H, H^7, *J* 4.89, 3.05 Hz), 3.99 m (2H, OCH_2), 3.73 m (2H, CH_2Cl), 3.25 d (1H, $H^4{}_e$, *J* 10.68 Hz), 3.25 d (1H, $H^2{}_e$, *J* 10.68 Hz), 3.10 d (1H, $H^9{}_e$, *J* 10.99 Hz), 2.88 br.d (1H, $H^8{}_e$, *J* 17.09 Hz), 2.72 d.d (1H, H_a^8, *J* 17.09, 4.88 Hz), 2.58 d (1H, H_a^9, *J* 10.99 Hz), 2.50 d (1H, H_a^2, *J* 10.68 Hz), 2.45 d (1H, H_a^4, *J* 10.68 Hz), 2.41 s (3H, N–CH_3). Found, %: C 43.30, 43.16; H 5.26, 5.11; N 13.52, 13.48; Cl 11.84, 11.71. $C_{11}H_{16}ClN_3O_5$. Calculated, %: C 43.22; H 5.28; N 13.74; Cl 11.62.

3-Methyl-1,5-dinitro-6-phenoxy-3-azabicyclo[3.3.1]non-6-ene (Ie). Yield 35%. Colorless crystals, mp 123–124°C. IR spectrum, cm^{-1}: 1692 (C=C), 1547, 1345 (NO_2), 1128 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.34 t (2H, $H^β$, *J* 8.10 Hz), 7.14 t (1H, $H^γ$, *J* 8.10 Hz), 7.04 t (2H, $H^α$, *J* 8.10 Hz), 5.25 d.d (1H, H^7, *J* 6.25, 1.97 Hz), 3.53 d (1H, H_e^4, *J* 11.16 Hz), 3.37 d (1H, H_e^2, *J* 10.5 Hz), 3.35 d (1H, H_e^9, *J* 11.6 Hz), 2.85 d.d (1H, H_e^8, *J* 17.72, 1.97 Hz), 2.74 d.d (1H, H_a^8, *J* 17.72, 6.25 Hz), 2.57 d (1H, H_a^9, *J* 11.6 Hz), 2.53 σ (3H, N–CH_3), 2.49 d (1H, H_a^2, *J* 10.5 Hz), 2.47 d (1H, H_a^4, *J* 11.16 Hz). Found, %: C 56.72, 56.73; H 5.30, 5.41;N13.10, 13.25. $C_{15}H_{17}N_3O_5$. Calculated, %: C 56.42; H 5.37; N 13.16.

6-Bromo-3-methyl-1,5-dinitro-3-azabicyclo-[3.3.1]non-6-ene (Ig). Yield 43%. Colorless crystals, mp 134–135°C. IR spectrum, cm^{-1}: 1646 (C=C), 1532, 1346 (NO_2). ^1H NMR spectrum (DMSO-d_6–CCl_4, 1:3), δ, ppm: 6.34 d.d (1H, H^7, *J* 4.89, 3.05 Hz), 3.25 d (1H, H_e^4, *J* 10.38 Hz), 3.15 d (1H, H_e^2, *J* 10.98 Hz), 3.14 d (1H, H_e^9, *J* 11.59 Hz), 2.97 br.d (1H, H_e^8, *J* 18.32 Hz), 2.77 d.d (1H, H_a^8, *J* 18.32, 4.89 Hz), 2.76 d (1H, H_a^9, *J* 11.59 Hz), 2.55 d (1H, H_a^2, *J* 10.98 Hz), 2.53 d (1H, H_a^4, *J* 10.38 Hz), 2.45 s (3H, N–CH_3). Found, %: C 35.96, 36.02; H 3.97, 4.11; N 13.48, 13.59; Br 26.01, 25.79. $C_9H_{12}BrN_3O_4$. Calculated, %: C 35.31; H 3.95; N 13.73; Br 26.14.

6(7)-R-3,3-Dimethyl-1,5-dinitro-3-azoniabicyclo-[3.3.1]non-6-ene iodides (IIa–i). To a solution of 0.4 mmol of an appropriate 1,5-dinitro-3-azabicyclo[3.3.1]-non-6-ene derivative **I** in a minimal amount of anhydrous acetonitrile was added 0.75 ml (12 mmol) of methyl iodide. The flask equipped with a reflux condenser was tightly stoppered and placed in the dark at 60°C for 48 h. The precipitated quaternary salt was filtered off and washed with a little acetonitrile.

3,3-Dimethyl-1,5-dinitro-3-azoniabicyclo-[3.3.1]non-6-ene iodide (IIa). Yield 73%, mp 184–186°C (decomp.). IR spectrum, cm^{-1}: 1542, 1342 (NO_2), 1671 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.28 br.s (1H, H^7), 4.29 d (1H, H_e^4, *J* 13.43 Hz), 2.54 d (1H, H_a^4, *J* 10.38 Hz), 3.115 d (1H, H_e^2, *J* 10.38 Hz), 4.16 d (1H, H_a^2, *J* 13.43 Hz), 3.11 d (1H, H_e^9, *J* 10.99 Hz), 2.99 d (1H, H_a^9, *J* 10.99 Hz), 3.20 d (1H, H_e^8, *J* 18.61 Hz), 3.08 d (1H, H_a^8, *J* 18.61 Hz), 3.44 s, 3.36 s (6H, N^+Me_2). Found, %: C 33.01, 32.79; H 4.37, 4.26; N 11.44, 11.50; I 33.94, 34.14. $C_{10}H_{16}IN_3O_4$. Calculated, %: C 32.52; H 4.34; N 11.38; I 34.42.

3,3,6-Trimethyl-1,5-dinitro-3-azoniabicyclo-[3.3.1]non-6-ene iodide (IIb). Yield 87%, mp 189–

191°C (decomp.). IR spectrum, cm^{-1}: 1571, 1343 (NO_2), 1642 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.01 br.s (1H, H^7), 4.47 d (1H, H^4_e, *J* 13.43 Hz), 4.02 d (1H, H^4_a, *J* 10.38 Hz), 4.27 d (1H, H^2_e, *J* 13.43 Hz), 4.11 d (1H, H^2_a, *J* 13.42 Hz), 3.13 d (1H, H^9_e, *J* 10.99 Hz), 3.07 d (1H, H^9_a, *J* 10.99 Hz), 3.21 d (1H, H^8_e, *J* 18.61 Hz), 3.04 d (1H, H^8_a, *J* 18.61 Hz), 3.41 s, 3.34 s (6H, N^+Me_2), 1.69 s (3H, CH_3). Found, %: C 34.37, 34.94; H 4.56, 4.82; N 11.60, 11.24; I 33.82, 33.89. $C_{11}H_{18}IN_3O_4$. Calculated, %: C 34.46; H 4.70; N 10.97; I 33.16.

3,3-Dimethyl-6-methoxy-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIc). Yield 95%, mp 173–175°C (decomp.). IR spectrum, cm^{-1}: 1570, 1358 (NO_2), 1685 (C=C), 1257 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.25 d.d (1H, H^7, *J* 4.88, 2.80 Hz), 4.35 d (1H, H^4_e, *J* 13.43 Hz), 4.05 d (1H, H^4_a, *J* 13.43 Hz), 4.31 d (1H, H^2_e, *J* 13.43 Hz), 4.17 d (1H, H^2_a, *J* 13.43 Hz), 3.22 d (1H, H^9_e, *J* 10.99 Hz), 3.11 d (1H, H^9_a, *J* 10.99 Hz), 3.24 d (1H, H^8_e, *J* 18.31 Hz), 3.04 d.d (1H, H^8_a, *J* 18.31, 4.88 Hz), 3.46 s, 3.40 s (6H, N^+Me_2), 3.65 s (3H, CH_3). Found, %: C 33.02, 33.09; H 4.60, 4.49; N 10.32, 10.30; I 31.46, 31.35. $C_{11}H_{18}IN_3O_5$. Calculated, %: C 33.08; H 4.51; N 10.53; I 31.83.

3,3-Dиmethyl-1,5-dinitro-6-(2-chloroetoxi)-3-azoniabicyclo[3.3.1]non-6-ene iodide (IId). Yield 83%, mp 166–168°C (decomp.). IR spectrum, cm^{-1}: 1554, 1338 (NO_2), 1675 (C=C), 1229 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.32 d.d (1H, H^7 *J* 4.88, 3.05 Hz), 4.29 d (1H, H^4_e, *J* 13.43 Hz), 4.06 d (1H, H^4_a, *J* 13.43 Hz), 4.29 d (1H, $H^2{}_e$, *J* 13.43 Hz), 4.21 d (1H, H^2_a, *J* 13.43 Hz), 3.25 d (1H, H^9_e, *J* 10.99 Hz), 3.14 d (1H, H^9_a, *J* 10.99 Hz), 3.28 d (1H, H^8_e, *J* 18.61 Hz), 3.01 d.d (1H, H^8_a, *J* 18.61, 4.88 Hz), 3.47 s, 3.38 s (6H, N^+Me_2), 3.82 t (2H, $\underline{CH_2}CH_2Cl$, *J* 4.88 Hz), 4.12 m (2H, $CH_2\underline{CH_2}Cl$). Found, %: C 32.07, 32.33; H 4.62, 4.58; N 10.96, 10.01; I 27.50, 27.47; Cl 7.41, 7.41. $C_{12}H_{19}ClIN_3O_5$. Calculated, %: C 32.18; H 4.25; N 9.39; I 28.38; Cl 7.93.

3,3-Dimethyl-1,5-dinitro-6-phenoxi-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIe). Yield 54%, mp 168–170°C (decomp.). IR spectrum, cm^{-1}: 1562, 1365 (NO_2), 1676 (C=C), 1222 (C–O). ^{1}H NMR spectrum NMR spectrum (DMSO-d_6), δ, ppm: 5.00 d.d (1H, H^7, *J* 4.88, 2.80 Hz), 4.66 d (1H, H^4_e, *J* 3.93 Hz), 4.11 d (1H, H^4_a, *J* 3.43 Hz), 4.35 d (1H, H^2_e, *J* 0.38 Hz), 4.33 d (1H, H^2_a, *J* 0.38 Hz), 3.34 d (1H, H^9_e, *J* 1.6 Hz), 3.25 d (1H, H^9_a, *J* 1.6 Hz), 3.21 d (1H, H^8_e, *J* 8.31 Hz), 2.3 d.d (1H, H^8_a, *J* 8.31, 4.89 Hz), 3.53 s, 3.52 s (6H N^+Me_2), 7.13 d (2H, H^α, *J* 7.93 Hz), 7.47 t (2H, H^β, *J* 7.93 Hz), 7.29 t (1H, H^γ, *J* 7.93 Hz). Found, %: C 41.86, 41.70; H 4.48, 4.52; N 9.10, 9.22; I 27.28, 27.68. $C_{16}H_{20}IN_3O_5$. Calculated, %: C 41.65; H 4.34; N 9.1; I 27.55.

3,3-Dimethyl-1,5-dinitro-6-chloro-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIf). Yield 45%, mp 172–174°C (decomp.). IR spectrum, cm^{-1}: 1569, 1367 (NO_2), 1630 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.74 d.d (1H, H^7, *J* 4.88, 3.05 Hz), 4.39 d (1H, H^4_e, *J* 13.43 Hz), 4.09 d (1H, H^4_a, *J* 13.43 Hz), 4.37 d (1H, H^2_e, *J* 13.43 Hz), 4.24 d (1H, H^2_a, *J* 13.43 Hz), 3.34 d (1H, H^9_e, *J* 11.59 Hz), 3.30 d (1H, H^9_a, *J* 11.6 Hz), 3.40 d (1H, H^8_e, *J* 18.92 Hz), 3.19 d.d (1H, H^8_a, *J* 18.92, 4.88 Hz), 3.51 s, 3.40 s (6H, N^+Me_2). Mass spectrum, *m/z*: 261 M^+, 250, 231, 214, 201, 200, 179, 168, 154, 150, 142, 134, 127, 118, 103, 100, 91, 77, 65, 51, 50, 42. Found, %: C 29.75, 29.94; H 3.82, 3.77; Cl 8.64, 8.67; I 30.92, 31.02; N 10.12, 10.18. $C_{10}H_{15}ClIN_3O_4$. Calculated, %: C 29.74; H 3.72; Cl 8.80; I 31.47; N 10.41.

6-Bromo-3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIg). Yield 42%, mp 180–182°C (decomp.). IR spectrum, cm^{-1}: 1567, 1365 (NO_2), 1635 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.57 d.d (1H, H^7, *J* 5.49, 3.05 Hz), 4.43 d (1H, H^4_e, *J* 13.42 Hz), 4.11 d (1H, H^4_a, *J* 13.42 Hz), 4.35 d (1H, H^2_e, *J* 13.42 Hz), 4.29 d (1H, H^2_a, *J* 13.42 Hz), 3.34 d (1H, H^9_e, *J* 11.6 Hz), 3.31 d (1H, H^9_a, *J* 11.6 Hz), 3.44 d (1H, H^8_e, *J* 18.92 Hz), 3.23 d.d (1H, H^8_a, *J* 18.92, 4.88 Hz), 3.50 s, 3.39 s (6H, N^+Me_2). Mass spectrum, *m/z*: 305 M^+, 280, 258, 245, 226, 212, 200, 172, 150, 142, 134, 127, 118, 103, 100, 91, 77, 65, 51, 50, 42. Found, %: C 26.98, 26.70; H 3.36, 3.43; Br 17.54, 17.61; I 27.85, 27.95; N 9.24, 9.08. $C_{10}H_{15}BrIN_3O_4$. Calculated, %: C 26.79; H 3.35; Br 17.86; I 28.35; N 9.38.

3,3-Dimethyl-7-methoxy-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIh). Yield 87%, mp 192–194°C (decomp.). IR spectrum, cm^{-1}: 1557, 1357 (NO_2), 1658 (C=C), 1242 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.32 br.s (1H, H^7), 4.30 d (1H, H^4_e, *J* 13.43 Hz), 4.06 d (1H, H^4_a, *J* 13.43 Hz), 4.19 d (1H, H^2_e, *J* 13.43 Hz), 4.16 d (1H, H^2_a, *J* 13.43 Hz), 3.10 d (1H, H^9_e, *J* 10.98 Hz), 3.01 d (1H, H^9_a, *J* 10.98 Hz), 3.30 d (1H, H^8_e, *J* 17.71 Hz), 3.04 d (1H, H^8_a, *J* 17.71 Hz), 3.66 s, 3.44 s (6H, N^+Me_2), 3.29 s (3H, CH_3). Found, %: C 33.40, 33.20; H 4.87, 4.96; I 31.61, 31.93; N 10.54, 10.58. $C_{11}H_{18}IN_3O_5$. Calculated, %: C 33.08; H 4.51; I 31.83; N 10.53.

7-Carbamoyl-3,3-dimethyl-1,5-dinitro-3-azoniabicyclo[3.3.1]non-6-ene iodide (IIi). Yield 46%, mp 202–204°C (decomp.). IR spectrum, cm^{-1}: 1572, 1358 (NO_2), 1657 (C=C), 1685 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.90 br.s (1H, H^7), 4.31 d (1H, H^4_e, *J* 13.43 Hz), 4.15 d (1H, H^4_a, *J* 13.43 Hz), 4.30 d (1H, H^2_e, *J* 12.81 Hz), 4.22 d (1H, H^2_a, *J* 12.81 Hz), 3.17 d (1H, H^9_e, *J* 11.59 Hz), 3.03 d (1H, H^9_a, *J* 11.59 Hz), 3.32 d (1H, H^8_e, *J* 18.32 Hz), 3.28 d (1H, H^8_a, *J* 18.32 Hz), 3.46 s, 3.29 s (6H, N^+Me_2), 7.75 br.s, 7.43 br.s (2H, $CONH_2$). Found, %: C 32.51, 32.80; H 4.30, 4.28; I 30.66, 30.27; N 12.64, 12.58. $C_{11}H_{17}IN_4O_5$. Calculated, %: C 32.04; H 4.13; I 30.83; N 13.59.

X-ray diffraction study of compound (IIa). The crystals were obtained by slow isothermal evaporation of compound **IIa** solution in ethanol. Crystals of $C_{10}H_{16}O_4N_3^+ I^-$ at 110(2) K monoclinic, *a* 8.051(3), *b* 10.679(3), *c* 8.635(3) Å, β 115.738(5)°, *V* 668.7(4) Å^3, crystal habit 0.3×0.3×0.2 mm, space group $P2_1$, *Z* 2, d_{calc} 1.833 g/cm^3, *F*(000) 364, m 2.406 mm^{-1}.

Intensities of 7351 reflections (3517 independent, R_{int} 0.021) were measured on an automatic diffractometer Bruker 1K SMART CCD (graphite monochromator, MoK_α-radiation, φ and ω scanning, $2\theta_{max}$ 58°). The processing of diffraction data was performed with software SAINT [20]. The absorption was taken into account with the use of software SADABS [21]. The structure was solved by the direct method applying the software package SHELXTL-97 [22]. Hydrogen atoms positions were revealed from the difference synthesis of the electron density and were refined in isotropic approximation except for atoms H attached to C^2 and C^4 atoms; these positions were calculated geometrically and refined in the *ritter* model with fixed U_{iso} 1.2 U_{eq} of the corresponding carbon atom. The refinement along F^2 in anisotropic approximation for nonhydrogen atoms by full-matrix least-squares procedure (219 parameters) involving 3517 reflections was carried out till *R*1 0.031 [for 3470 reflections with $F > 4y(F)$], *wR*2 0.083, *S* 1.078. The coordinates of nonhydrogen atoms are listed in Table 1, and the bond lengths in Table 2.

Zefirov–Palyulin folding parameters were calculated by RICON routine [23].

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