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STUDY OF THE BROMINATION OF 1,5-DINITRO-3-AZABICYCLO-[3.3.1]NON-6-ENES

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The electrophilic addition of bromine to 3-substituted 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene in carbon tetrachloride is accompanied by intramolecular 3,7-cyclization with the formation of 6-bromo-3-R-1,5-dinitro-3-azonia-tricyclo[3.3.$10^{3,7}$]nonane tribromides. In the bromination of 1,5-dinitro-3-aza-bicyclo[3.3.1]non-6-enes containing substituents at the double bond, molecular complexes of halogen with the substrate were obtained.

Keywords: 3-azabicyclo[3.3.1]non-6-enes, homo- and heteronuclear correlation spectroscopy, halogenation.

Derivatives of azabicyclo[3.3.1]nonane possess various biological activities [1-3], consequently broadening the range of compounds of this class is urgent and offers promise for the directed synthesis of biologically active substances and the study of structure–activity relationships. One of the methods of functionalizing the derivatives of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes previously synthesized by us [4-8] may be the addition of electrophilic reagents at the double bond. It was shown previously that electrophilic addition of halogenating agents to 2-azanorborn-5-ene leads to the formation of rearranged products [9, 10], and addition of bromine and dihalogen iodates to 2-alkyl-2-azabicyclo[2.2.1]hept-5-ene and 2-alkyl-2-azabicyclo-[2.2.2]oct-5-ene leads to a quaternary ammonium salt containing an aziridinium ring [11, 12]. The reactivity of the double bond towards electrophilic interaction in 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes is reduced due to the influence of the electron-withdrawing 5-NO_2 group. In addition, steric factors characteristic of the framework of the system introduce their own contribution to deactivation. In this connection, as a model permitting study of the reactivity of the C=C double bond of the cyclohexene fragment of the bicyclic system, we selected the bromination reaction which has not been described for compounds of this type up to the present time.

It was established that in the reaction of an excess of bromine with 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **1a-l** in CCl_4, 3-R-6-bromo-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$]nonane tribromides **2a-l** were isolated in quantitative yield as orange solids readily soluble in water, in place of the expected products of addition of halogen at the double bond, 3-R-6,7-dibromo-1,5-dinitro-3-azabicyclo[3.3.1]nonanes (**B**). The obtained compounds **2a-l** have the structure of quaternary salts and contain the complex tribromide anion,as indicated by

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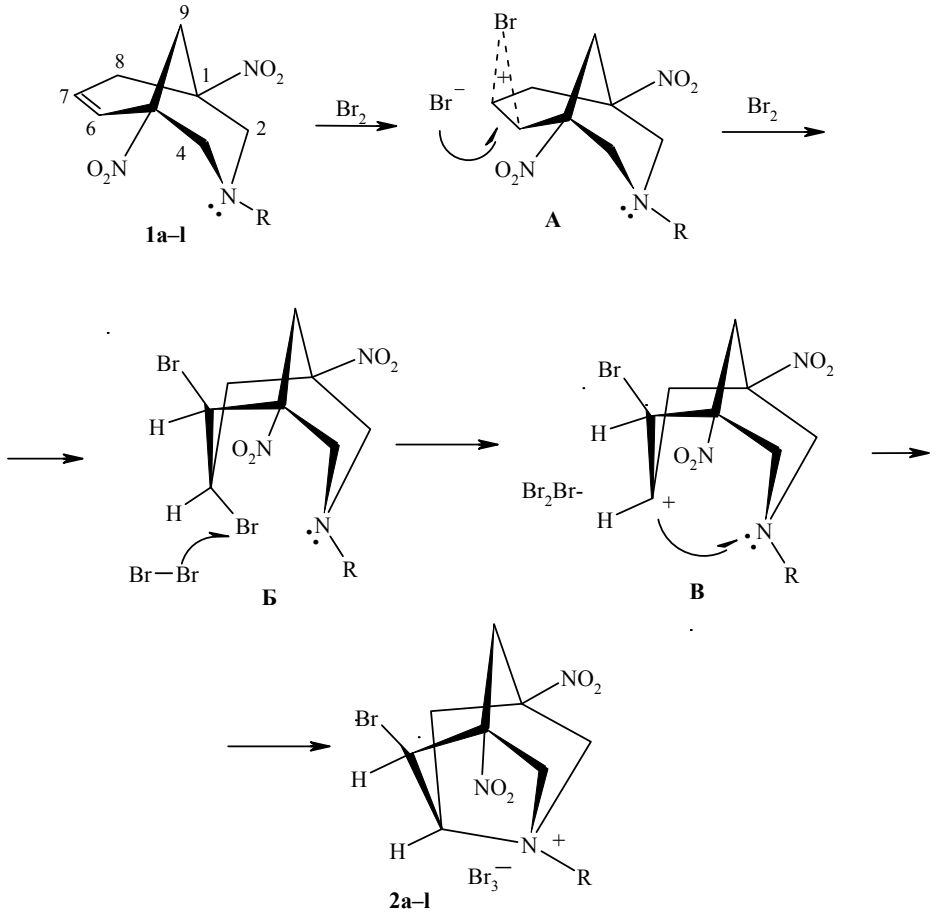
the character of their IR and NMR spectra and data of elemental analysis. Intense bands for the stretching vibrations of nitro groups were detected in the IR spectra of the compounds at 1550-1600 and 1350-1370, and bands of medium strength at 760-680 cm^{-1} corresponding to the vibrations of a C-Br bond [13]. The absence from the spectra of bands for the stretching vibrations of the C=C bond indicates the saturated character of compounds **2a-l**.



1, 2 a R = Me, **b** R = Et, **c** R = Pr, **d** *i*-Pr, **e** R = Bu, **f** R = *n*-C_5H_{11},
g R = *i*-C_5H_{11}, **h** R = $(CH_2)_2OH$, **i** R = $CH(C_2H_5)CH_2OH$,
j R = $(CH_2)_2Br$, **k** R = CH_2Ph, **l** R = 1-bicyclo[2.2.1]heptylethyl

For a more precise assignment of signals in the NMR spectra of the synthesized compounds the two-dimensional correlation NMR spectra (HSQC, HMBC, COSY, NOESY) of 6-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$]nonane tribromide (**2a**) and of the initial compound **1a** were recorded. The ^{1}H NMR spectrum of compound **2a** is a complex ten-spin system, however analysis of it is simplified by the presence in the molecule of the $C_{(7)}$-$N_{(3)}$ bond, thanks to which the piperidine and cyclohexane rings are clearly fixed in a *chair–chair* conformation (Table 1).

A starting point for interpreting the NMR spectra may be served by the low field broadened doublet (5.73 ppm, ^3J = 6.62 Hz) of the H-6 proton at the carbon atom directly linked with halogen, and the singlet of the N-methyl group protons at 3.59 ppm, which have correlation peaks $^1J_{CH}$ in the 2D HSQC spectrum with the signals of the carbon atoms at 53.06 and 55.01 respectively, and also cross peaks $^2J_{CH}$ in the HMBC spectrum H-6/$C_{(7)}$, H-6/$C_{(5)}$ and $^3J_{CH}$ H-6/$C_{(9)}$, H-6/$C_{(8)}$, Me/$C_{(4)}$, Me/$C_{(2)}$, and Me/$C_{(7)}$ (Table 2). The presence of a vicinal coupling constant between the protons of the methyl group and the $C_{(7)}$ atom indicates the formation in the

molecule of a covalent bond between the $C_{(7)}$-$N_{(3)}$ atoms. The signal of the H-7 proton is observed in the ^{1}H NMR spectrum as a triplet (5.18 ppm, ^3J = 6.62 Hz) as a result of the concurrence of the vicinal constants from the interaction with the neighboring H-6 and H-8 atoms. Assignment of the signal of the H-7 proton was confirmed by the presence of the corresponding correlation peaks in the heteronuclear correlation HSQC (H-7/$C_{(7)}$, 81.45 ppm) and HMBC (H-7/$C_{(1)}$, H 7/$C_{(5)}$, and H-7/NMe) spectra.

The signals of the quaternary $C_{(5)}$ and $C_{(1)}$ atoms at 90.04 and 88.18 ppm respectively, having no cross peaks in the HSQC spectrum, may differ in coupling constant in the HMBC spectrum $^2J_{CH}$ H-6/$C_{(5)}$, $^3J_{CH}$ H-4e/$C_{(5)}$, H-2e/$C_{(1)}$, and H-8e/$C_{(1)}$ (Table 2). The positive charge on the nitrogen atom of the piperidine ring of

TABLE 1. ^{1}H NMR Spectra of Compounds **1a** and **2a**

Atom	Chemical shifts, δ, ppm (*J*Hz)*	
	1a	**2a**
H-2*e*	3.10 (d, *J* = 10.61)	4.42 (d, *J* = 10.98)
H-2*a*	2.48 (d, *J* = 10.61)	4.31 (dd, *J* = 10.98, *J* = 1.84)
H-4*e*	3.30 (d, *J* = 10.53)	4.50 (dd, *J* = 11.03, *J* = 1.84)
H-4*a*	2.46 (d, *J* = 10.53)	4.62 (d, *J* = 11.03)
H-6	5.95 (d, *J* = 10.0)	5.73 (d, *J* = 6.62)
H-7	6.06 (dt, *J* = 10.0, *J* = 2.52)	5.18 (t, *J* = 6.62)
H-8*endo* (H-8*e*)	2.80 (dd, *J* = 17.0, *J* = 2.52)	3.24 (ddd, *J* = 13.61, *J* = 7.73, *J* = 1.47)
H-8*exo* (H-8*a*)	2.47 (d, *J* = 17.0)	3.14 (dd, *J* = 13.61, *J* = 2.22)
H-9*e* (H-8*exo*)	2.85 (d, *J* = 11.0)	3.18 (d, *J* = 13.23)
H-9*a* (H-9*endo*)	2.63 (d, *J* = 11.0)	3.41 (d, *J* = 13.23)
NMe	2.43 (s)	3.44 (s), 3.59 (c)

*^{1}H NMR spectra were taken on Bruker DRX 500 (500 MHz) (compound **1a**) and Bruker AC 300 (300 MHz) (compound **2a**) instruments.

TABLE 2. ^{13}C NMR Spectra* and Correlation Peaks in HMBC Spectra of Compounds **1a** and **2a**

Atom	δ_C, ppm	HMBC	δ_C, ppm	HMBC
	1a		**2a**	
$C_{(1)}$	86.89	H-2*e*, H-2*a*, H-8*endo*, H-8*exo*, H-9*e*, H-9*a*	82.89	H-2*e*, H-8*e*, H-7
$C_{(2)}$	64.06	H-4*e*, H-4*a*, H-8*endo*, H-9*e*, H-9*a*	69.70	NMe, H-4*e*, H-4$_a$, H-8*a*, H-9*exo*
$C_{(4)}$	60.43	NMe, H-2*e*, H-8*exo*, H-9*e*, H-9*a*	67.28	NMe, H-2*e*, H-2*a*, H-9*exo*
$C_{(5)}$	84.45	H-4*e*, H-4*a*, H-6, H-9*e*, H-9*a*	84.72	H-4*e*, H-6, H-7
$C_{(6)}$	125.63	H-4*e*, H-4*a*, H-8*endo*, H-8*exo*, H-9*a*	47.72	H-9*endo*
$C_{(7)}$	129.71	H-8*exo*, H-8*endo*	76.27	NMe, H-2*a*, H-4*a*, H-6
$C_{(8)}$	36.52	H-7, H-9*a*	36.15	H-6, H-9*endo*
$C_{(9)}$	37.22	H-2*e*, H-2*a*, H-4*e*, H-4*a*	30.78	H-6
NMe	45.01	H-2*a*	49.68	H-7

*^{13}C NMR spectra were taken on Bruker DRX 500 (125 MHz) (compound **1a**) and Bruker AC 300 (75 MHz) (compound **2a**) instruments.

compound **2a** causes a strong displacement towards low field (Δδ ~1.0 ppm) of the signals of the H-2 and H-4 methylene protons and of the N-methyl group in comparison with the signals of the analogous protons of the initial substrate **1a** (Table 1), which confirms the structure of the quaternary ammonium salt.

The H-2 and H-4 protons in compound **2a** are diastereotopic and form a group of four doublet signals with geminal constant ^2J = 11 Hz in the 4.3-4.6 ppm region. The signals of the equatorial protons H-4*e* and H-2*e* are broadened due to the *W* interaction (width at half height $W_{½}$ 4.0-4.4 Hz), but each component of the doublet of the axial H-2*a* proton is split further into a doublet with ^4J = 1.84 Hz as a result of the long range interaction with proton H-8*a*. The corresponding *W* constants of the equatorial protons H-2*e*, H-4*e*, H-9*exo*, and also the coupling constant ^4J H-2*a*/H-8*a* are well seen in the ^{1}H-^{1}H homonuclear COSY correlation spectrum. The signals of the $C_{(2)}$ and $C_{(4)}$ atoms (75.0 and 72.56 ppm respectively) were readily determined from the HSQC spectrum and from the $^3J_{CH}$ H-2*e*/$C_{(4)}$, H-2*a*/$C_{(4)}$, NMe/$C_{(4)}$, H-9*exo*/$C_{(4)}$, H-4*a*/$C_{(2)}$, H-4e/$C_{(2)}$, NMe/$C_{(2)}$, H-9*exo*/$C_{(2)}$, and H-8*a*/$C_{(2)}$ constants in the HMBC spectrum (Table 2). Like the H-2 and H-4 protons, the signals of atoms $C_{(2)}$, $C_{(4)}$, and the NMe group were displaced by 6-7 ppm towards low field in comparison with the ^{13}C NMR spectrum of the initial bicyclononane **1a** (Table 2). It is important to note the presence in the HMBC spectrum of correlation peaks through three bonds of the axial H-2*a* and H-4*a* with the $C_{(7)}$ atom, which also indicates the formation of the $C_{(7)}$-$N_{(3)}$ bond.

The broadened doublets at 3.41 and 3.18 ppm (^2J = 13.23 Hz, width at half line height $W_{½}$ 4.41 Hz) correspond to the signals of the bridge protons H-9*endo* and H-9*exo* respectively. Since these protons are common to the two rings and occupy an equatorial position in one and an axial in the other, to distinguish them is possible from the $^3J_{CH}$ H-9*endo*/$C_{(8)}$, H-9*endo*/$C_{(6)}$, H-9*exo*/$C_{(4)}$, H-9*exo*/$C_{(2)}$ cross peaks in the HMBC spectrum (Table 2), and also with the aid of the $^4J_{HH}$ H-6*e*/H-9*endo*, H-4*e*/H-9*exo*, and H-2*e*/H-9*exo* correlation peaks in the COSY spectrum.

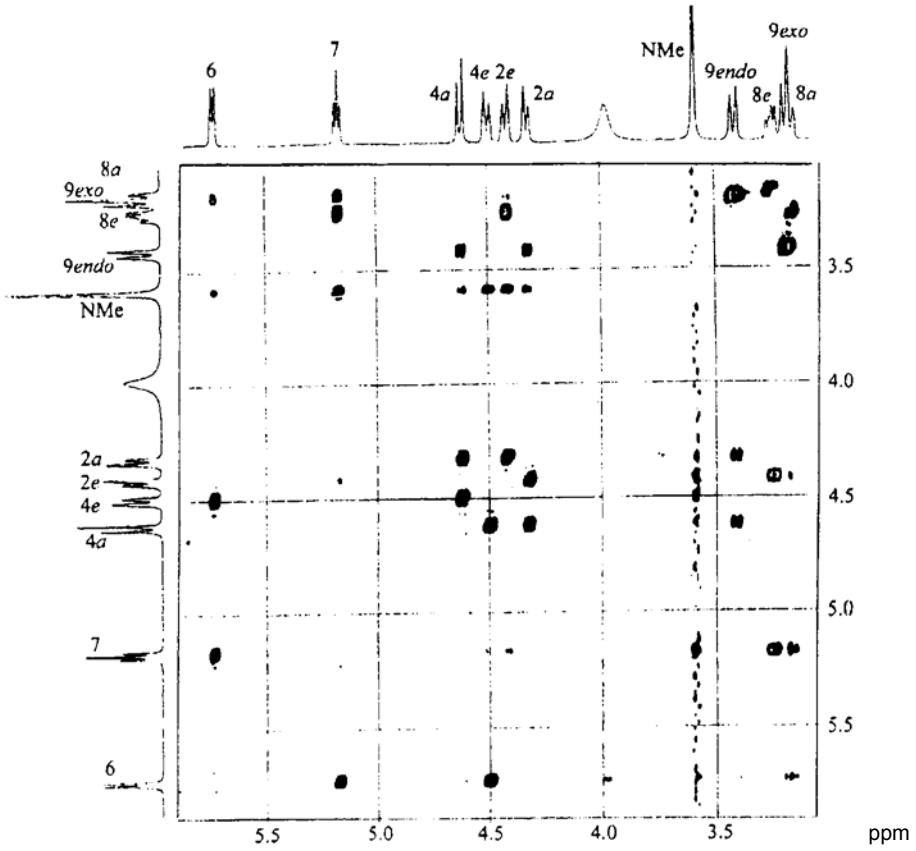


Fig. 1. Two-dimensional ^{1}H-^{1}H correlation NOE spectrum (NOESY) of 6-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane tribromide (**2a**).

Finally, the signal of the H-8*e* equatorial proton is split into a doublet of doublets of doublets ^2J = 13.6, ^3J = 7.73, ^4J = 1.47 Hz), and the signal of the H-8*a* proton into a doublet of doublets (^2J = 13.6, ^4J = 2.2 Hz) and were detected at 3.24 and 3.14 ppm respectively. Assignment of the signal at high field at 3.24 to the H-8*a* proton is based on the presence of *W* constants with the H-2*a* proton in the COSY spectrum.

The equatorial H-8*e* proton, according to data of quantum chemical calculations of the cation of compound **2a** by the PM3 method [14], is found at a distance of 2.47 Å from the H-2*e* proton. Consequently an Overhauser effect must be observed for these protons, which was confirmed by a NOESY experiment (Fig. 1). The NOE spectrum indicates the close disposition of the axial protons H-2*a*, H-4*a*, and H-9*endo* of the piperidine ring, and confirms its chair-like conformation. The correlation peak in the proton spectrum for H-7 and the N-methyl group protons also indicates their spatial proximity, and consequently the presence of the $C_{(7)}$–$N_{(3)}$ bond (calculated interproton distance H-7–Me 2.62 Å). We note the absence of double bond carbon atom signals in the 120-140 ppm region in the ^{13}C NMR spectrum of compound **2a**.

The problem of the stereochemistry of the $C_{(6)}$ atom in the molecule of 6-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane tribromide (2a) must be considered separately. This compound has several chiral centers in its structure ($C_{(1)}$, $N_{(3)}$, $C_{(5)}$, $C_{(6)}$, and $C_{(7)}$), and consequently may exist in the form of several diastereoisomers. However, one set of signals was observed in the NMR spectra, which indicates the isolation of one stereoisomer. The following data indicate the axial disposition of the bromine atom in the cyclohexane fragment (6*S* configuration). In the COSY spectrum, the cross peak, caused by the *W* interaction of the H-9*endo* and H-6 protons, which assumes an equatorial orientation for the latter, is fixed by the homonuclear ^{1}H-^{1}H correlation. In the NOESY spectrum (Fig. 1), a correlation peak is observed for the H-4*e* and H-6 protons caused by the proximity of their disposition to one another. It is known that the Overhauser effect is displayed for atoms located at a distance of 2.0-3.0 Å from one another [15]. Optimization of the geometry of cation **2a** with equatorial and axial orientation of the bromine atom in position 6 by the PM3 method gives a value for the interatomic H-6—H-4*e* distances of 3.81 and 2.49 Å respectively. Consequently a NOE effect is possible in the case of a diequatorial disposition of the H-6*e* and H-4*e* atoms.

Analysis of the data of NMR spectroscopy therefore permits the conclusion that the compound being investigated is the tribromide of 6*S*-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3,3,1,0^{3,7}]nonane, the formation of which in all probability occurs as a result of the conversions given in the scheme. The addition of halogen in the first stage may occur with the formation of both a classic carbocation and an ion of bridge structure **A**. Analysis of the NMR spectra showed that the 6*S* stereoisomer was obtained as a result, i.e. the product of *anti* addition. Consequently the cation formed on attack by bromine of the azabicyclononene molecule may be assigned to the bridge structure **A** [9]. In the 6,7-dibromo derivative **B** the spatial structure of the cyclohexane fragment is reduced as a result of saturation. From a sofa conformation it passes over to the energetically more favorable chair conformation, which makes sterically possible a 3,7-cyclization as a result of intramolecular alkylation of the piperidine ring nitrogen atom in carbocation **C**. Formation of the latter occurs with the assistance of a second molecule of bromine, which assists fission of bromide ion from the dibromo derivative **B** by forming the complex Br_3^- cation, i.e. a trimolecular mechanism occurs in the reaction, as a result of which the final compound **2** is isolated as a quaternary bromonium salt. It is impossible to exclude the possibility of the reaction also proceeding through the formation at the first stage of a classical carbocation of type **C**, which assists polarization of the double bond under the action of an allylic nitro group. However in this case the stereoselectivity of the process is significantly less [9].

The conformational changes occurring on bromination of 3-aza-bicyclo[3.3.1]non-6-ene must be reflected in the geometric parameters of the molecule. Results are given in Table 3 of calculations by the PM3 method of some valence angles in the molecules of compounds **1a** and **2a**. It follows from the obtained data that the valence angles $C_{(4)}$–$C_{(5)}$–$C_{(6)}$, $C_{(5)}$–$C_{(4)}$–$N_{(3)}$, and particularly $C_{(5)}$–$C_{(6)}$–$C_{(7)}$ are strongly reduced, which is in agreement with the conformational transition of the cyclohexene fragment from sofa into a chair-like saturated six-membered ring. It is interesting that the valence angle $C_{(1)}$–$C_{(9)}$–$C_{(5)}$ is increased by this, while the $C_{(2)}$–$N_{(3)}$–$C_{(4)}$ angle is reduced.

TABLE 3. Some Valence Angles (ω) in the Molecules of Compound **1a** and Tribromide **2a**, Calculated by the PM3 Method

Angle	ω, deg	
	1a	**2a**
$C_{(1)}$–$C_{(9)}$–$C_{(5)}$	108.72	111.83
$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	108.74	99.15
$C_{(5)}$–$C_{(4)}$–$N_{(3)}$	109.99	100.72
$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	121.44	101.47
$C_{(2)}$–$N_{(3)}$–$C_{(4)}$	112.96	104.58

It was established that the nature of the solvent has a strong influence on the course of this reaction. Bromination of 3-azabicyclo[3.3.1]non-6-ene (**1a**) in low-polarity solvents (benzene, dichloroethane) at various temperatures (from 5°C to the boiling point of the solvent) leads to the formation of tribromide **2a** in 68-96% yield. On carrying out the reaction in methanol with 1 equiv. bromine the solution was decolorized, however no solid precipitated. On adding a 1.5-fold excess of Br_2 the solution acquired a light orange coloration and precipitation of a white crystalline solid began, the yield of which was 63%. The IR and NMR spectra of the isolated compound have practically the same set of signals as 6-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$]nonane tribromide (**2a**), however according to data of elemental analysis this substance contains two atoms of bromine, and has a different melting point. It follows from this that the obtained substance is 6-bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$] nonane bromide (**3a**). On carrying out the reaction in acetonitrile a mixture of the mono- and tribromides is formed. The results obtained show that in a polar solvent bromination combined with 3,7 cyclization leads directly to the monobromide **3**. Participation of the solvent in this process may therefore be effected at the stage of forming carbocation **C** through polarization of the C-Br bond in the dibromo derivative **B**. Furthermore the complex Br^{3-} anion is decomposed in polar media, which assists the formation of monobromides. It is interesting that the monobromide is formed in dioxane through the ability of the latter to form covalent compounds with molecular bromine [16], which also leads to decomposition of the tribromide anion.

On treating compounds **2a-l** with polar solvents (acetone, methanol) bromides of 6-bromo-3-R-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$]nonanes **3a-l** are formed in quantitative yield. Transition of tribromides into monobromides may also be effected by heating 6-bromo-3-R-1,5-dinitro-3-azoniatricyclo[3.3.1.$0^{3,7}$]nonanes above 130°C. Substances lose their orange color and their mass is reduced by this, which indicates decomposition of the tribromide anion.

In connection with the obtained data on the bromination of 3-azabicyclo-[3.3.1]non-6-ene derivatives, the problem arises of the effect of substituents at the double bond (positions 6 or 7 of the substrate) on the process being investigated. It might be suggested that the reaction will be hampered for steric reasons in this case. On reacting molecular bromine with solutions of 6-chloro- and 7-methoxycarbonyl-1,5-dinitro-3-aza-bicyclo[3.3.1]non-6-enes in CCl_4 an orange solid was precipitated from the reaction solution, suggesting in outward appearance the tribromides of the azoniatricyclo[3.3.1.$0^{3,7}$]nonanes described above. However the results of elemental analysis showed that the compounds isolated contain only two atoms of bromine. Analysis of the NMR spectra of the obtained compounds showed their unsaturated character. In the ^{1}H NMR spectrum absorption was observed for olefinic protons at 6.0-6.75 ppm, and in the ^{13}C NMR spectrum signals at 125-135 ppm correspond to atoms at a C=C bond. These data enable the conclusion to be drawn that the electrophilic addition of halogen at the double bond of these substrates does not occur. It is also known that in the reaction of tertiary amines with molecular bromine in CCl_4 the formation of halides of quaternary N-haloammonium halides is possible [17]. However the formation of a similar series of salts in the bromination of 6(7)-substituted 3-azabicyclo[3.3.1]non-6-enes was not detected, as indicated by the insignificant displacement of chemical

shifts of the signals in the NMR spectra of the isolated reaction products in comparison with the initial substrates ($\Delta\delta_H$ 0.1-0.2, $\Delta\delta_C$ 0.1-0.2 ppm). The exceptions are only the signals of the H-2*a* and H-4*a* protons (low field displacement by 0.8-1.0 ppm), which are in the *trans* diaxial position relative to the unshared electron pair of the nitrogen atom. Therefore in the reaction of bromine on solutions of 6(7)-substituted compounds in CCl_4, in all probability, molecular complexes are formed in which azabicyclononanes act as donor and halogen as acceptor of the unshared electron pair of the heteroatom.

EXPERIMENTAL

The IR spectra (nujol or film from acetone) were recorded on a Specord IR 75 spectrometer. The NMR spectra were recorded on Bruker DRX 500, Bruker AC 300, Bruker WM 250 and Bruker AC 200 spectrometers in DMSO-d_6, internal standard was HMDS. The purity and identity of compounds were checked by TLC (Silufol UV 254, eluent toluene–acetone–hexane, 1:4:1, detection in UV light). The melting points of compounds were measured on a Boetius Kofler stage. Quantum-chemical calculations were carried out on a PC (550 MHz) using the HyperChem 6.0 set of programs. Optimization algorithm was Polak-Ribiere, RMS gradient 10^{-5}.

The initial compounds **1a-l** were obtained by the procedures described previously in [4-8].

Preparation of Tribromides 2a-l (general Method). A solution of bromine (0.044 ml: 0.88 mmol) in absolute CCl_4 (5 ml) was added dropwise to a solution of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-ene in CCl_4 (5 ml). The precipitated orange solid was filtered off, washed with a small amount of CCl_4, and dried in a vacuum desiccator to constant mass.

6-Bromo-3-methyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2a). Mp 131-132°C (decomp.); yield 95%. IR spectrum, ν, cm^{-1}: 2700 (C-N$^+$), 1561, 1366 (NO_2), 710 (C-Br), 1260 (CH_3). Found, %: C 19.43; H 2.23; Br 58.21; N 7.24. $C_9H_{13}Br_4N_3O_4$. Calculated, %: C 19.74; H 2.38; Br 58.50; N 7.68.

6-Bromo-3-ethyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2b). Mp 135-136°C (decomp.); yield 94%. IR spectrum, ν, cm^{-1}: 2726 (C-N$^+$), 1553, 1373 (NO_2), 720 (C-Br), 1263 (CH_3). ^{1}H NMR spectrum (250 Hz), δ, ppm (*J*, Hz): 5.27 (1H, br. s, H-7); 5.73 (1H, d, *J* = 6.1, H-6); 4.48 (1H, d, *J* = 10.98, H-4*e*); 4.70 (1H, d, *J* = 10.98, H-4*a*); 4.39 (2H, br. s, H-2*e*, H-2*a*); 3.22 (1H, d, *J* = 12.82, H-9*exo*); 3.40 (1H, d, *J* = 12.82, H-9*endo*); 3.19 (2H, br. s, H-8*e*, H-8*a*); 3.59 (2H, m, CH_2CH_3); 1.33 (3H, t, *J* = 6.72, CH_2CH_3). ^{13}C NMR spectrum (63 MHz), δ, ppm : 83.95 ($C_{(1)}$); 66.62 ($C_{(2)}$); 64.84 ($C_{(4)}$); 84.84 ($C_{(5)}$); 47.58 ($C_{(6)}$); 75.27 ($C_{(7)}$); 35.79 ($C_{(8)}$); 31.34 ($C_{(9)}$); 57.98 (CH_2); 8.59 (CH_3). Found, %: C 21.62; H 2.34; Br 56.73; N 7.87. $C_{10}H_{15}Br_4N_3O_4$. Calculated, %: C 21.39; H 2.67; Br 57.04; N 7.49.

6-Bromo-1,5-dinitro-3-propyl-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2c). Mp 136-137°C (decomp.); yield 98%. IR spectrum, ν, cm^{-1}: 2729 (C-N$^+$), 1600, 1327 (NO_2), 760 (C-Br), 1275 (CH_3). ^{1}H NMR spectrum (250 MHz), δ, ppm (*J*, Hz): 5.29 (1H, m, H-7); 5.69 (1H, d, *J* = 6.72, H-6); 4.51 (1H, d, *J* = 10.99, H-4*e*); 4.69 (1H, d, *J* = 10.99, H-4*a*); 4.39 (1H, d, *J* = 11.15, H-2*a*); 4.43 (1H, d, *J* = 11.15, H-2*e*); 3.22 (1H, d, *J* = 13.23, H-9*exo*); 3.39 (1H, d, *J* = 13.23, H-9*endo*); 3.19 (2H, br. s, H-8*e*, H-8*a*); 3.83 (2H, m, $C\underline{H}_2CH_2CH_3$); 1.73 (2H, m, $CH_2C\underline{H}_2CH_3$); 0.93 (3H, t, *J* = 7.32, $CH_2CH_2C\underline{H}_3$); 3.59 (3H, s, CH_3). ^{13}C NMR spectrum (63 MHz), δ, ppm: 83.09 ($C_{(1)}$); 67.16 ($C_{(2)}$); 65.25 ($C_{(4)}$); 84.89 ($C_{(5)}$); 47.49 ($C_{(6)}$); 75.96 ($C_{(7)}$); 35.79 ($C_{(8)}$); 31.25 ($C_{(9)}$); 63.43 (NCH_2); 16.39 (CH_2); 10.42 (CH_3). Found, %: C 22.64; H 2.83; Br 55.52; N 7.22. $C_{11}H_{17}Br_4N_3O_4$. Calculated, %: C 22.96; H 2.96; Br 55.65; N 7.30.

6-Bromo-3-isopropyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2d). Mp 136-137°C (decomp.); yield 98%. IR spectrum, ν, cm^{-1}:2726 (C-N$^+$), 1562, 1360 (NO_2), 726 (C-Br), 1230 (CH_3). ^{1}H NMR spectrum (250 MHz), δ, ppm (*J*, Hz): 5.42 (1H, t, *J* = 7.02, H-7); 5.68 (1H, d, *J* = 6.71, H-6); 4.44 (1H, d, *J* = 10.68, H-4*e*); 4.79 (1H, d, *J* = 10.68, 4*a*); 4.35 (2H, br. s, H-2*e*, H-2*a*); 3.24 (1H, d, *J* = 12.6, H-9*exo*); 3.42

(1H, d, *J* = 12.6, H-9*endo*); 3.07 (1H, d d, *J* = 12.82, *J* = 6.71, H-8*e*); 3.20 (1H, d, *J* = 12.82, H-8*a*); 4.3 [1H, m, C<u>H</u>$(CH_3)_2$]; 1.41, 1.39 [6H, d, *J* = 5.8, CH(C<u>H</u>$_3)_2$]. ^{13}C NMR spectrum (63 MHz), δ, ppm: 83.17 ($C_{(1)}$); 64.88 ($C_{(2)}$); 63.59 ($C_{(4)}$); 84.88 ($C_{(5)}$); 47.55 ($C_{(6)}$); 73.75 ($C_{(7)}$); 35.62 ($C_{(8)}$); 32.04 ($C_{(9)}$); 63.28 (NCH), 16.52 (CH_3); 16.45 (CH_3). Found, %: C 22.75; H 2.65; Br 55.83; N 7.23. $C_{11}H_{17}Br_4N_3O_4$. Calculated, %: C 22.96; H 2.96; Br 55.65; N 7.30.

6-Bromo-3-butyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2e). Mp 134-135°C (decomp.); yield 92%. IR spectrum, ν, cm^{-1}: 2720 (C-N$^+$), 1533, 1353 (NO_2), 727 (C-Br). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.29 (1H, t, *J* = 6.15, H-7); 5.75 (1H, d, *J* = 6.42, H-6); 4.53 (1H, d, J = 10.82, H-4*e*); 4.74 (1H, d, *J* = 10.82, H-4*a*); 4.43 (2H, br. s, H-2*e,a*); 3.21 (1H, d, *J* = 13.02, H-9*exo*); 3.40 (1H, d, *J* = 13.02, H-9*endo*); 3.20 (1H, d, *J* = 13.39, H-8*e*); 3.17 (1H, d, *J* = 13.39, H-8*a*); 3.91 [2H, m, C<u>H</u>$_2(CH_2)_2CH_3$]; 1.70 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 1.34 (2H, m, $CH_2CH_2C\underline{H}_2CH_3$); 0.94 (3H, t, *J* = 7.33, $CH_2CH_2CH_2C\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 83.0 ($C_{(1)}$); 66.91 ($C_{(2)}$); 65.0 ($C_{(4)}$); 84.79 ($C_{(5)}$); 47.49 ($C_{(6)}$); 75.86 ($C_{(7)}$); 35.69 ($C_{(8)}$); 31.19 ($C_{(9)}$); 61.89 [<u>C</u>$H_2(CH_2)_2CH_3$]; 24.38 ($CH_2\underline{C}H_2CH_2CH_3$); 18.99 ($CH_2CH_2\underline{C}H_2CH_3$); 13.32 ($CH_2CH_2CH_2\underline{C}H_3$). Found, %: C 24.13; H 3.03; Br 54.15; N 6.74. $C_{12}H_{19}Br_4N_3O_4$. Calculated, %: C 24.45; H 3.23; Br 54.33; N 7.13.

6-Bromo-1,5-dinitro-3-pentyl-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2f). Mp 133-134°C (decomp.); yield 96%. IR spectrum, ν, cm^{-1}: 2730 (C-N$^+$), 1554, 1345 (NO_2), 713 (C-Br), 1254 (CH_3). ^{1}H NMR spectrum (250 MHz), δ, ppm (*J*, Hz): 5.29 (1H, m, H-7); 5.74 (1H, d, *J* = 6.1, H-6); 4.53 (1H, d, *J* = 10.99, H-4*e*); 4.73 (1H, d, *J* = 10.99, H-4*a*); 4.43 (2H, br. s, H-2*e*, H-2*a*); 3.22 (1H, d, *J* = 12.6, H-9*exo*); 3.37 (1H, d, *J* = H-9*endo*); 3.19 (2H, br. s, H-8*e*, H-8*a*); 3.91 [2H, m, C<u>H</u>$_2(CH_2)_3CH_3$]; 1.71 [2H, m, $CH_2C\underline{H}_2(CH_2)_2CH_3$]; 1.34 [4H, m, $(CH_2)_2C\underline{H}_2C\underline{H}_2CH_3$]; 0.91 (3H, t, *J* = 6.71. CH_3]. ^{13}C NMR spectrum (63 MHz), δ, ppm: 83.11 ($C_{(1)}$); 67.01 ($C_{(2)}$); 65.12 ($C_{(4)}$); 84.89 ($C_{(5)}$); 47.55 ($C_{(6)}$); 75.92 ($C_{(7)}$); 35.77 ($C_{(8)}$); 31.29 ($C_{(9)}$); 27.74 (N<u>C</u>H_2); 27.74 (<u>C</u>H_2); 22.24 (<u>C</u>H_2); 21.59 (<u>C</u>H_2); 13.76 (<u>C</u>H_3). Found, %: C 25.72; H 3.45; Br 53.45; N 6.72. $C_{13}H_{21}Br_4N_3O_4$. Calculated, %: C 25.87; H 3.48; Br 53.07; N 6.96.

6-Bromo-3-isopentyl-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2g). Mp 135-136°C (decomp.); yield 95%. IR spectrum, ν, cm^{-1}: 2725 (C-N$^+$), 1544, 1359 (NO_2), 705 (C-Br), 1232 (CH_3). ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 5.29 (1H, t, *J* = 6.35, H-7); 5.83 (1H, d, *J* = 6.35, H-6); 4.54 (1H, d, *J* = 10.74, H-4*e*); 4.80 (1H, d, *J* = 10.47, H-4*a*); 4.43 (1H, d, *J* = 10.75, H-2*e*); 4.48 (1H, d, *J* = 10.75, H-2*a*); 3.20 (1H, d, *J* = 12.69, H-9*exo*); 3.44 (1H, d, *J* = 12.69, H-9*endo*); 3.28 (1H, d d, *J* = 13.18, *J* = 7.32, H-8*e*); 3.17 (1H, d, *J* = 13.0, H-8*a*); 4.0 (2H, m, NC<u>H</u>$_2$); 1.63 [3H, m, $NCH_2C\underline{H}_2C\underline{H}(CH_3)_2$]; 0.96, 0.93 [6H, s, $NCH_2CH_2CH(C\underline{H}_3)_2$]. ^{13}C NMR spectrum (50 MHz), δ, ppm: 82.99 ($C_{(1)}$); 66.71 ($C_{(2)}$); 64.81 ($C_{(4)}$); 84.75 ($C_{(5)}$); 47.42 ($C_{(6)}$); 76.0 ($C_{(7)}$); 35.64 ($C_{(8)}$); 31.22 ($C_{(9)}$); 61.07 (N<u>C</u>H_2); 30.67 [$NHCH_2CH_2\underline{C}H(CH_3)_2$]; 25.59 [$NCH_2\underline{C}H_2CH(CH_3)_2$]; 21.98 [$NCH_2CH_2CH(\underline{C}H_3)_2$]. Found, %: C 25.67; H 3.34; Br 52.89; N 6.78. $C_{13}H_{21}Br_4N_3O_4$. Calculated, %: C 25.87; H 3.48; Br 53.07; N 6.96.

6-Bromo-3-(2-hydroxyethyl)-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2h). Mp 132-133°C; yield 93%. IR spectrum, ν, cm^{-1}: 2722 (C-N$^+$), 1552, 1360 (NO_2), 715 (C-Br), 3272 (OH). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.32 (1H, t, *J* = 6.03, H-7); 5.72 (1H, d, *J* = 5.67, H-6); 4.56 (1H, d, *J* = 11.2, H-4*e*); 4.70 (1H, d, *J* = 11,2, H-4*a*); 4,37 (1H, d, *J* = 10.99, H-2*a*); 4.47 (1H, d, *J* = 10.99, H-2*e*); 3.21 (1H, d, *J* = 12.62, H-9*exo*); 3.43 (1H, d, *J* = 12.62, H-9*endo*); 3.19 (2H, br. s, H-8*e*, H-8*a*); 5.62 (1H, br. s, OH); 4.01 (2H, m, C<u>H</u>$_2CH_2OH$); 3.9 (2H, m, $CH_2C\underline{H}_2OH$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 82.97 ($C_{(1)}$); 68.18 ($C_{(2)}$); 66.4 ($C_{(4)}$); 84.79 ($C_{(5)}$); 47.53 ($C_{(6)}$); 77.01 ($C_{(7)}$); 35.72 ($C_{(8)}$); 31.12 ($C_{(9)}$); 64.09 (<u>C</u>H_2OH); 55.37 (NCH_2). Found, %: C 20.94; H 2.78; Br 55.72; N 7.56. $C_{10}H_{15}Br_4N_3O_5$. Calculated, %: C 20.80; H 2.60; Br 55.46; N 7.28.

6-Bromo-3-(1-hydroxy-2-butyl)-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]-nonane Tribromide (2i). Mp 137-138°C (decomp.); yield 90%. IR spectrum, ν, cm^{-1}:2700 (C-N$^+$), 1561, 1366 (NO_2), 710 (C-Br), 1260 (CH_3). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.56, 5.50 (1H, t, *J* = 6.78, H-7); 5.68, 5.62 (1H, d, *J* = 6.78, H-6); 4.63, 4,42 (1H, d, *J* = 11.0, H-4*e*); 4.78, 4.73 (1H, d, *J* = 11.0, H-4*a*); 4.40 (1H, d, *J* = 10.46,

H-2*e*); 4.56 (1H, d, *J* = 10.46, H-2*a*); 3.18 (1H, d, *J* = 13.0, H-9*exo*); 3.40 (1H, d, *J* = 13.0, H-9*endo*); 3.16 (2H, m, H-8*e,a*); 4.03 (1H, t, *J* = 12.29, OH); 3.96, 3.83 (2H, d d, t d, *J* = 13.93, *J* = 5.5, *J* = 3.3, C$\underline{H}_2$OH); 3.45 [1H, m, NC$\underline{H}$(C_2H_5)CH_2OH]; 1.85, 1.72 (2H, m, C$\underline{H}_2$$CH_3$); 1.00 (3H, t, *J* = 7.06, CH_2C$\underline{H}_3$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 83.21, 82.87 ($C_{(1)}$); 75.86, 75.71 ($C_{(2)}$); 65.34, 64.37 ($C_{(4)}$); 84.69, 84.55 ($C_{(5)}$); 47.62, 47.60 ($C_{(6)}$); 75.86, 75.71 ($C_{(7)}$); 35.88, 35.55 ($C_{(8)}$); 31.96, 31.64 ($C_{(9)}$); 74.17, 74.01 (CH_2OH); 56.63, 56.19 (N$\underline{C}$H); 18.42, 18.31 ($\underline{C}H_2CH_3$); 10.50, 10.44 ($CH_2\underline{C}H_3$). Found, %: C 23.67; H 3.42; Br 52.64; N 6.72. $C_{12}H_{19}Br_4N_3O_5$. Calculated, %: C 23.80; H 3.14; Br 52.89; N 6.94.

6-Bromo-3-(2-bromoethyl)-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2j). Mp 138-139°C (decomp.); yield 94%. IR spectrum, ν, cm^{-1}: 2727 (C-N$^+$), 1561, 1367 (NO_2), 680 (C-Br). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.43 (1H, t, *J* = 6.0, H-7), 5.72 (1H, d, *J* = 6.0, H-6); 4.62 (1H, d, *J* = 11.0, H-4*e*); 4.74 (1H, d, *J* = 11.0, H-4*a*); 4.47 (1H, d, *J* = 11.0, H-2*e*); 4.51 (1H, d, *J* = 11.0, H-2*a*); 3.21 (1H, d, *J* = 13.0, H-9*exo*); 3,48 (1H, d, *J* = 13.0, H-9*endo*); 3.20 (2H, br. s, H-8*e,a*); 4.42 (2H, t, CH_2C$\underline{H}_2$Br); 3.98 (2H, m, C$\underline{H}_2$$CH_2$Br). ^{13}C NMR spectrum (126 MHz), δ, ppm: 82.99 ($C_{(1)}$); 67.43 ($C_{(2)}$); 65.47 ($C_{(4)}$); 84.71 ($C_{(5)}$); 47.12 ($C_{(6)}$); 76.82 ($C_{(7)}$); 35.63 ($C_{(8)}$); 31.05 ($C_{(9)}$); 61.44 ($\underline{C}H_2CH_2$Br); 22.54 ($CH_2\underline{C}H_2$Br). Found, %: C 18.62; H 2.08; Br 62.23; N 6.34. $C_{10}H_{14}Br_5N_3O_4$. Calculated, %: C 18.75; H 2.19; Br 62.50; N 6.56.

3-Benzyl-6-bromo-1,5-dinitro-3-azoniatricyclo[3.3.1.0^{3,7}]nonane Tribromide (2k). Mp 138-139°C (decomp.); yield 93%. IR spectrum, ν, cm^{-1}: 2719 (C-N$^+$), 1540, 1356 (NO_2), 740 (C-Br), 690 (CH_{arom}), 1600 (C=C). ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 5.18 (1H, m, H-7); 5.5 (1H, t, *J* = 6.03, H-6); 4.19 (1H, d, *J* = 10.43, H-4*e*); 4.85 (1H, q, *J* = 10.43, H-4*a*); 3.88 (1H, d, *J* = 9.88, H-2*a*); 4.72 (1H, q, *J* = 9.88, H-2*e*); 3.18 (1H, d, *J* = 12.62, H-9*exo*); 3.26 (1H, d, *J* = 12.62, H-9*endo*); 3.27 (2H, br. s, H-8*e*, H-8*a*); 7.71, 7.57 (5H, m, C_6H_5); 5.84, 5.24 (2H, m, $CH_2C_6H_5$). ^{13}C NMR spectrum (126 MHz), δ, ppm: 82.77 ($C_{(1)}$); 66.88 ($C_{(2)}$); 66.67 ($C_{(4)}$); 84.78 ($C_{(5)}$); 47.37 ($C_{(6)}$); 75.91 ($C_{(7)}$); 36.01 ($C_{(8)}$); 30.89 ($C_{(9)}$); 131.81, 130.79, 129.43, 127.57, 64.59 ($CH_2C_6H_5$). Found, %: C 28.87; H 2.43; Br 51.32; N 6.54. $C_{15}H_{17}Br_4N_3O_4$. Calculated, %: C 28.89; H 2.73; Br 51.36; N 6.74.

3-{α-(2-Bicyclo[2.2.1]heptyl)ethyl}-6-bromo-1,5-dinitro-3-azoniatricyclo-[3.3.1.0^{3,7}]nonane Tribromide (2l). Mp 140-141°C (decomp.); yield 93%. IR spectrum, ν, cm^{-1}: 2721 (C-N$^+$), 1538, 1352 (NO_2), 716 (C-Br), 1240 (CH_3). ^{1}H NMR spectrum (250 MHz), δ, ppm (*J*, Hz): 5.42, 5.38 (1H, t, *J* = 6.71 H-7); 5.68, 5.60 (1H, d, *J* = 6.71, H-6); 4.60, 4.40 (1H, d, *J* = 11.0, H-4*e*); 4.80, 4.70 (1H, d. *J* = 11.0, H-4*a*); 4.34 (2H, m, H-2*e,a*); 3.20 (1H, d, *J* = 13.0, H-9*exo*); 3.40 (1H, d, *J* = 13.0, H-9*endo*); 3.20 (2H, m, H-8*e,a*); 4.28 (1H, m, NC$\underline{H}$); 1.48, 1.45 (3H, d, *J* = 5.5, NCHC$\underline{H}_3$); 1.3 (m, C_7H_{11}). ^{13}C NMR spectrum (63 MHz), δ, ppm: 83.30, 83.16 ($C_{(1)}$); 72.41, 69.99 ($C_{(2)}$); 66.13, 62.73 ($C_{(4)}$); 84.86, 84.79 ($C_{(5)}$); 47.19, 47.06 ($C_{(6)}$); 75.43, 75.40 ($C_{(7)}$); 35.49, 35.44 ($C_{(8)}$); 29.77, 29.48 ($C_{(9)}$); 43.77 (NCH); 14.64 (CH_3); 39.71, 39.38, 38.02, 36.90, 32.22, 22.41, 22.04 (C_7H_{11}). Found, %: C 30.89; H 3.56; Br 48.56; N 6.34. $C_{17}H_{25}Br_4N_3O_4$. Calculated, %: C 31.15; H 3.82; Br 48.85; N 6.41.

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