Halogenation of 2-alkyl-2-azabicycloalkenes as a method for the synthesis of stable aziridinium salts of a new class

S. E. Sosonyuk, M. N. Bulanov, I. F. Leshcheva, and N. V. Zyk*

Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob´evy Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 0290. E-mail: ses@org.chem.msu.su

Addition of bromine and potassium dihaloiodates(I) to 2-alkyl-2-azabicyclo[2.2.1]hept-5-enes and 2-alkyl-2-azabicyclo[2.2.2]oct-5-enes affords quaternary ammonium salts containing the aziridine ring and the polyhalide anion. The possibility of using these salts for the synthesis of 6-substituted 2-alkyl-2-azabicyclo[2.2.1]heptanes has been shown.

Key words: 2-azabicyclo[2.2.1]heptenes, 2-azabicyclo[2.2.2]octenes, 1-azoniatricyclo[2.2.1.$0^{2,6}$]heptanes, 1-azoniatricyclo[3.2.1.$0^{2,7}$]octanes, 2-azabicyclo[2.2.1]heptanes, aziridines, quaternary ammonium salts, polyhalides, halogenation.

Aziridinium ions as nitrogen-containing analogs of epoxides are a promising but inadequately studied class of organic compounds. This explains why these compounds have been given more interest in recent years.[1] However, the majority of relevant studies are devoted to the synthesis of unstable aziridinium ions and their subsequent *in situ* opening. Only salts with nonnucleophilic anions such as perchlorate and tetrafluoroborate have been isolated in the individual state.[2]

For this reason, a new class of stable aziridinium salts with polyhalide anions as counterions, obtained by us by halogenation of *N*-alkylazanorbornenes, is of special interest.[3] Earlier,[4] it was shown that the bromination of azanorborn-5-enes exclusively affords rearranged products. However, that study was concerned only with nonsubstituted and acylated derivatives of this azabicycloolefin. Electrophilic addition to *N*-alkylazanorbornenes has not been studied to date.

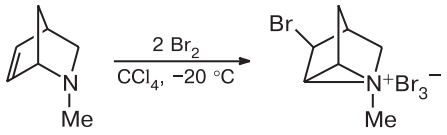
Results and Discussion

In an attempt[3] to add bromine to *N*-methyl-5-azanorbornene (**1a**), we unexpectedly obtained a product containing four Br atoms per one molecule of the starting olefin. A quantitative yield was reached with the use of a double excess of bromine. The structure of 3-bromo-1-methyl-1-azoniatricyclo[2.2.1.$0^{2,6}$]heptane tribromide (**2a**) was assigned to the reaction product (Scheme 1).

The goal of the present work was to confirm the structures of the salts obtained and extend their range. Four azabicyclic olefins (**1a—c**, **3**) synthesized as described in Ref. 5 were chosen as substrates (Scheme 2).

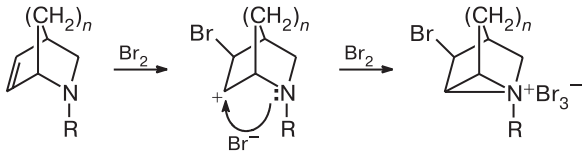
These substrates were halogenated with three reagents, namely, bromine, potassium dichloroiodate(I),[6] and potassium dibromoiodate(I).[7]

Scheme 1



1a **2a**

Scheme 2



1a—c, **3** **2a—c**, **4a**

Compound	*n*	R
1a, **2a**	1	Me
1b, **2b**	1	Et

Compound	*n*	R
1c, **2c**	1	Bn
3, **4a**	2	Me

In all cases, bromination of substrates **1a—c** and **3** in CCl_4 gave quaternary ammonium salts (**2a—c**, **4a**) containing a three-membered aziridine ring and a complex tribromide anion rather than adducts of two bromine atoms at the double bond (or rearrangement products[4]). Some salts were obtained in nearly quantitative yields.

Obviously, the bromination of *N*-alkylazabicyclic olefins follows Scheme 2.

Both the possibility of obtaining tribromides and their yields were found to be largely influenced by the solvent polarity and the temperature. The best results were obtained for bromination in CCl_4 at −20 °C. In chloroform or methylene chloride, the expected adducts undergo

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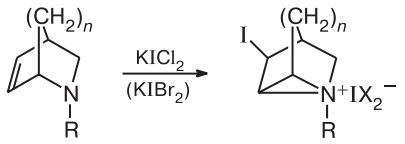
resinification; bromination in methanol gives the adducts in lower yields.

Iodochlorination and iodobromination of azabicyclic olefins (Scheme 3) was carried out in ice-cooled chloroform. The reaction products were corresponding quaternary ammonium dichloroiodates (**2d—f**, **4b**) and dibromoiodates (**2g—i**, **4c**). All adducts (**2a—i**, **4a—c**) are brightly colored crystalline substances stable in storage.

Scheme 3



1a—c, **3** **2d—i**, **4b**,**c**

Compound	*n*	R	X	Compound	*n*	R	X
2d	1	Me	Cl	**2h**	1	Et	Br
2e	1	Et	Cl	**2i**	1	Bn	Br
2f	1	Bn	Cl	**4b**	2	Me	Cl
2g	1	Me	Br	**4c**	2	Me	Br

The structure of compound **2d** was determined from X-ray diffraction data (Fig. 1); it was confirmed that its molecule contains an aziridine ring and a linear dichloroiodate(I) anion. All signals were assigned in the ^{1}H and ^{13}C NMR spectra of compound **2d**. A series of H-{^{1}H} double resonance experiments were performed for its ^{1}H NMR spectra. The orientation of the H(5) (*syn*, *anti*) and H(7) protons (*exo*, *endo*) was determined from long-range W-coupling constants. To assign signals

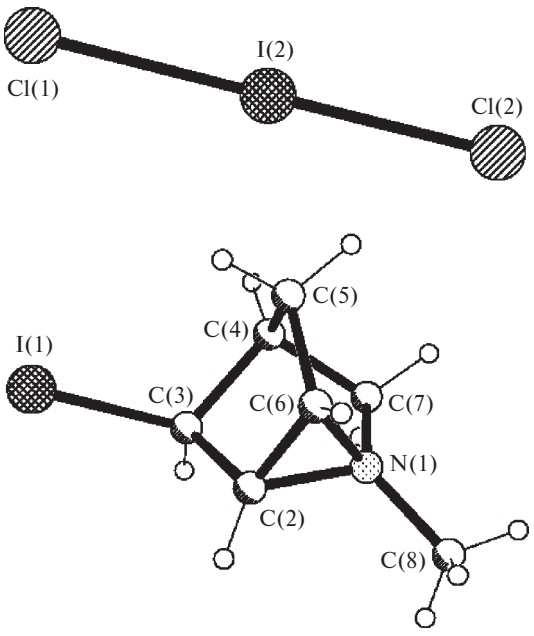
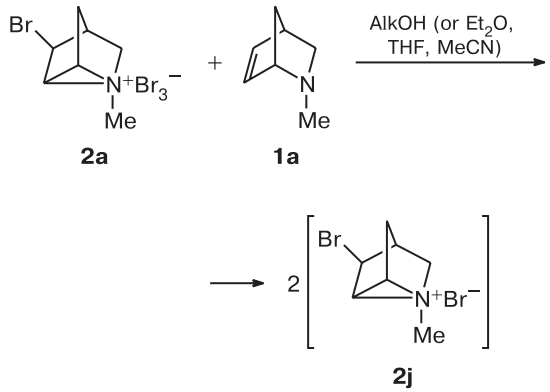


Fig. 1. Structure **2d** (according to the X-ray diffraction data).

in the ^{13}C NMR spectrum, ^{13}C NMR spectra without proton decoupling and with selective decoupling from the H(2), H(3), and H(6) protons were recorded. The spectra are completely consistent with the structure proposed. Because of a positive charge at the nitrogen atom, all signals in the ^{1}H and ^{13}C NMR spectra are shifted downfield compared to the spectra of neutral compounds, especially signals for the atoms adjacent to the N atom, *i.e.*, C(2), C(6), and C(7), and for the C atom in the alkyl substituent and signals for the corresponding protons. The NMR spectra of all compounds of this series are virtually identical with the ^{1}H and ^{13}C NMR spectra of compound **2d**, except signals for the substituent at the N atom. Based on this similarity, one can assign analogous structures to the compounds obtained. It should be noted that the spectra of dichloroiodates **2d**, **2e**, and **4b** are identical with the spectra of the corresponding dibromoiodates **2g**, **2h**, and **4c**, *i.e.*, the spectrum of the compound is insensitive to the anion nature.

While studying the reactivities of the salts obtained, we found that tribromide **2a** reacts with one equivalent of the starting olefin **1a** in a polar solvent (ethanol, ether, tetrahydrofuran, or acetonitrile) to give a decolorized solution. The colorless solid substance isolated from the reaction mixture was unstable in air. It turned out that its ^{1}H NMR spectrum contains the same set of signals as the ^{1}H NMR spectrum of **2a**. This enabled us to conclude that the isolated product is the corresponding monobromide **2j** (Scheme 4).

Scheme 4

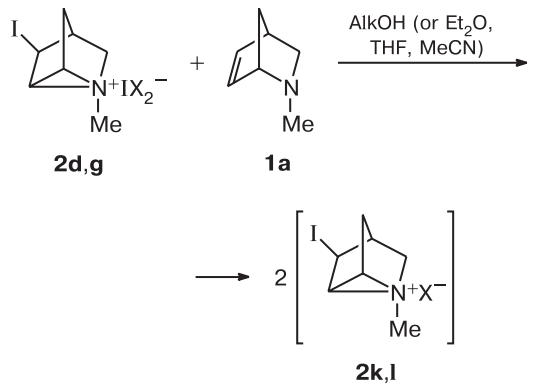


Having isolated monobromide **2j**, we attempted the synthesis of this compound by brominating the starting methylazanorbornene **1a** in acetonitrile to skip the formation of tribromide **2a**. However, product **2j** contained an impurity of tribromide and was not isolated in the individual state.

Analogously, the reactions of compounds **2d** and **2g** with one equivalent of **1a** yielded unstable chloride **2k** and bromide **2l**, respectively. Their ^{1}H NMR spectra are

identical with each other and similar to the spectrum of compound **2j** (Scheme 5).

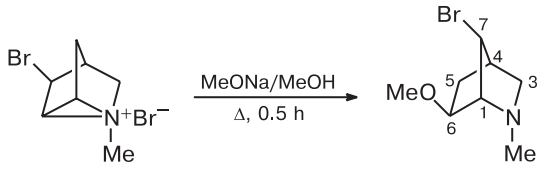
Scheme 5



2d,**g** **1a** **2k**,**l**

Aziridine derivatives are valuable reagents for organic synthesis, first of all, because of the possibility of nucleophilic opening of their rings. We found that the reaction of compound **2j** with sodium methoxide in boiling methanol affords 7-bromo-6-methoxyazanorbornane (**5**), which can be isolated as hydrochloride in 57% yield (Scheme 6).

Scheme 6



2j **5**

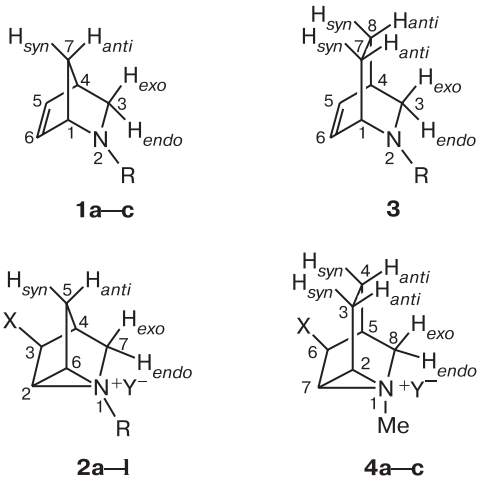
The configuration of compound **5** was determined from ^{1}H NMR data. Irradiation of a signal for the H(7) proton gave W-coupling constants with the *endo*-H(5) and H(6) protons (each constant is 1.3 Hz), which indicates the *exo-syn*-arrangement of the substituents.

Hence, stable aziridinium salts **2a**—**i** and **4a**—**c** can be obtained by halogenation of azanorbornene derivatives. The nucleophilic opening of the aziridine ring makes it possible to synthesize 6-substituted 2-alkyl-2-azanorbornanes.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (in $CDCl_3$ for compounds **1a**—**c**, **3**, and **5** and in CD_3CN for compounds **2a**—**l** and **4a**—**c**) at 28 °C with $SiMe_4$ as the internal standard. Chemical shifts are given on the δ scale (ppm); spin-spin coupling constants (*J*) are expressed in Hz. Signals in the ^{1}H NMR spectra were assigned using the H-{^{1}H} double resonance method and compared with the literature data.[8,9] In some cases, ^{13}C NMR spectra were interpreted by editing them with the APT sequence.

Chemical shifts and coupling constants for the ^{1}H and ^{13}C NMR spectra of the compounds obtained are given in Tables 1—3. Elemental analysis data for compounds **2a**—**i** and **4a**—**c** are presented in Table 4.



1a—c **3** **2a—l** **4a—c**

Single crystals of compound **2d** were obtained by crystallization from ethanol. X-ray diffraction analysis was carried out on a Bruker SMART 1000 CCD diffractometer (graphite monochromator, λ(Mo-K_α) = 0.71073 Å, ω scan mode) at 150 K. Crystallographic parameters and a summary of data collection for compound **2d** are given in Table 5. An absorption correction was determined experimentally from the azimuthal scan curves (T_{min}/T_{max}). The structure was solved by the direct method. The coordinates and thermal parameters of non-hydrogen atoms were refined by the full-matrix least-squares method in the isotropic and then anisotropic approximation. Hydrogen atoms were located geometrically and refined in the riding model. All calculations were performed with the SHELXL-97 program package.

Synthesis of the starting azabicycloolefins (general procedure) (*cf.* Ref. 5). A mixture of a diene, an amine hydrochloride, and 37% formalin (all reagents were taken in the amounts specified below) was stirred at a specified temperature for a specified period of time. When the diene was taken in an excess, its excess was removed by double extraction with light petroleum. Then a cooled 10% NaOH solution (1.5 equiv. with respect to the amine) was added to the stirred aqueous solution. The organic layer was separated, and the organic material was extracted three times from the aqueous phase with ether. The combined organic extracts were dried with anhydrous sodium sulfate, the ether was removed, and the product was distilled in an atmosphere of argon.

2-Methyl-2-azabicyclo[2.2.1]hept-5-ene (1a) was obtained according to the general procedure from freshly distilled cyclopentadiene (15.5 mL, 188 mmol), 37% formalin (20 mL, 247 mmol of formaldehyde), and methylamine hydrochloride (16.7 g, 247 mmol). The reaction was carried out at ~20 °C for 3 h. The yield of compound **1a** was 16.0 g (78%), b.p. 37 °C (60 Torr), n_D^{24} 1.4473 (see Ref. 10).

2-Ethyl-2-azabicyclo[2.2.1]hept-5-ene (1b) was obtained analogously from freshly distilled cyclopentadiene (15.5 mL, 188 mmol), 37% formalin (20 mL, 247 mmol of formaldehyde), and ethylamine hydrochloride (20.1 g, 247 mmol). The yield of compound **1b** was 15.6 g (67%), b.p. 147—150 °C

Table 1. ^{1}H and ^{13}C NMR spectra of compounds **1a—c** and **3**

Compound	H(1), C(1)	H(3), C(3)	H(4), C(4)	H(5), C(5)	H(6), C(6)	H(7), C(7), H(8), C(8)	H(R), C(R)
1a	3.70 (dt, 1 H, H(1), $J_{H(1),H(6)} = 3.1$, $J_{H(1),H_{syn}(7)} = 1.4$, $J_{H(1),H_{anti}(7)} = 1.4$)	3.12 (dd, 1 H, $H_{exo}(3)$, $J_{H_{exo}(3),H_{endo}(3)} = 8.4$, $J_{H_{exo}(3),H(4)} = 3.0$); 1.32 (dd, 1 H, $H_{endo}(3)$, $J_{H_{endo}(3),H_{exo}(3)} = 8.4$, $J_{H_{endo}(3),H(4)} = 1.7$)	2.86 (m, 1 H, H(4))	6.00 (dd, 1 H, H(5), $J_{H(5),H(6)} = 5.7$, $J_{H(5),H(4)} = 2.1$)	6.29 (ddd, 1 H, H(6), $J_{H(6),H(5)} = 5.7$, $J_{H(6),H(1)} = 3.1$, $J_{H(6),H_{anti}(7)} = 1.4$)	1.56 (dt, 1 H, $H_{syn}(7)$, $J_{H_{syn}(7),H_{anti}(7)} = 8.1$, $J_{H_{syn}(7),H(1)} = 1.4$, $J_{H_{syn}(7),H(4)} = 1.4$); 1.36 (dq, 1 H, $H_{anti}(7)$, $J_{H_{anti}(7),H_{syn}(7)} = 8.1$, $J_{H_{anti}(7),H(1)} = 1.4$, $J_{H_{anti}(7),H(4)} = 1.4$, $J_{H_{anti}(7),H(6)} = 1.4$);	2.13 (s, 3 H, H(Me))
	65.6 (C(1))	52.9 (C(3))	40.6 (C(4))	130.1 (C(5))	136.0 (C(6))	48.2 (C(7))	43.9 (C(Me))
1b	3.87 (m, 1 H, H(1))	3.13 (dd, 1 H, $H_{exo}(3)$, $J_{H_{exo}(3),H_{endo}(3)} = 8.7$, $J_{H_{exo}(3),H(4)} = 3.0$); 1.43 (dd, 1 H, $H_{endo}(3)$, $J_{H_{endo}(3),H_{exo}(3)} = 8.7$, $J_{H_{endo}(3),H(4)} = 1.7$)	2.89 (m, 1 H, H(4))	5.98 (dd, 1 H, H(5), $J_{H(5),H(6)} = 5.7$, $J_{H(5),H(4)} = 2.1$)	6.30 (ddd, 1 H, H(6), $J_{H(6),H(5)} = 5.7$, $J_{H(6),H(1)} = 3.1$, $J_{H(6),H_{anti}(7)} = 1.1$)	1.57 (dt, 1 H, $H_{syn}(7)$, $J_{H_{syn}(7),H_{anti}(7)} = 8.2$, $J_{H_{syn}(7),H(1)} = 1.6$, $J_{H_{syn}(7),H(4)} = 1.6$); 1.39 (dq, 1 H, $H_{anti}(7)$, $J_{H_{anti}(7),H_{syn}(7)} = 8.2$, $J_{H_{anti}(7),H(1)} = 1.6$, $J_{H_{anti}(7),H(4)} = 1.6$, $J_{H_{anti}(7),H(6)} = 1.6$)	2.38 (dq, 2 H, $\underline{CH_2}$Me, H(Et), $J_{H,H'} = 11.8$, $J_{H,Me} = 7.3$); 1.05 (т, 3 H, $CH_2\underline{Me}$, H(Et), $J = 7.3$)
1c	3.78 (m, 1 H, H(1))	3.14 (dd, 1 H, $H_{exo}(3)$, $J_{H_{exo}(3),H_{endo}(3)} = 8.7$, $J_{H_{exo}(3),H(4)} = 3.1$); 1.49 (dd, 1 H, $H_{endo}(3)$, $J_{H_{endo}(3),H_{exo}(3)} = 8.7$, $J_{H_{endo}(3),H(4)} = 1.7$)	2.89 (m, 1 H, H(4))	6.05 (dd, 1 H, H(5), $J_{H(5),H(6)} = 5.8$, $J_{H(5),H(4)} = 2.1$)	6.34 (ddd, 1 H, H(6), $J_{H(6),H(5)} = 5.8$, $J_{H(6),H(1)} = 3.0$, $J_{H(6),H_{anti}(7)} = 1.1$)	1.61 (dt, 1 H, $H_{syn}(7)$, $J_{H_{syn}(7),H_{anti}(7)} = 8.1$, $J_{H_{syn}(7),H(1)} = 1.6$, $J_{H_{syn}(7),H(4)} = 1.6$); 1.38 (dq, 1 H, $H_{anti}(7)$, $J_{H_{anti}(7),H_{syn}(7)} = 8.1$, $J_{H_{anti}(7),H(1)} = 1.6$, $J_{H_{anti}(7),H(4)} = 1.6$, $J_{H_{anti}(7),H(6)} = 1.6$)	7.17—7.34 (m, 5 H), H($\underline{CH_2}$Ph, H(arom.)); 3.54, 3.31 (both d, 1 H each, H(CH_2Ph), $J_{H,H'} = 13.1$)
3	3.24 (m, 1 H, H(1))	3.01 (dd, 1 H, $H_{exo}(3)$, $J_{H_{exo}(3),H_{endo}(3)} = 9.7$, $J_{H_{exo}(3),H(4)} = 2.2$); 1.85 (dt, 1 H, $H_{endo}(3)$, $J_{H_{endo}(3),H_{exo}(3)} = 9.7$, $J_{H_{endo}(3),H(4)} = 2.6$, $J_{H_{endo}(3),H_{syn}(8)} = 2.6$)	2.45 (m, 1 H, H(4))	6.35 (dd, 1 H, H(5), $J_{H(5),H(6)} = 8.2$, $J_{H(5),H(4)} = 6.8$)	6.24 (dd, 1 H, H(6), $J_{H(6),H(5)} = 8.2$, $J_{H(6),H(1)} = 5.4$)	1.96 (ddt, 1 H, $H_{syn}(7)$, $J_{H_{syn}(7),H_{anti}(7)} = 11.8$, $J_{H_{syn}(7),H_{syn}(8)} = 9.5$, $J_{H_{syn}(7),H_{anti}(8)} = 3.2$, $J_{H_{syn}(7),H(1)} = 3.2$); 1.28 (m, 1 H, $H_{anti}(7)$, $J_{H_{anti}(7),H_{syn}(7)} = 11.8$); 1.50, 1.18 (both m, 1 H each, H(8));	2.19 (s, 3 H, H(Me));
	56.6 (C(1))	54.1 (C(3))	31.1 (C(4))	133.4 (C(5))	131.7 (C(6))	21.8 (C(8)); 26.9 (C(7))	45.2 (C(Me))

Table 2. ^{1}H and ^{13}C NMR spectra of compounds **2a—l**

Compound	H(2), C(2)	H(3), C(3)	H(4), C(4)	H(5), C(5)	H(6), C(6)	H(7), C(7)	H(R), C(R)
2a	4.03 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 2.0)	4.49 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 2.0)	2.89 (m, 1 H, (H(4))	2.39 (d, 1 H, H_{syn}(5), $J_{H_{syn}(5),H_{anti}(5)}$ = 13.3); 2.30 (dd, 1 H, H_{anti}(5), $J_{H_{anti}(5),H_{syn}(5)}$ = 13.3, $J_{H_{anti}(5),H(6)}$ = 1.7)	3.95 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.24 (dd, 1 H, H_{exo}(7), $J_{H_{exo}(7),H_{endo}(7)}$ = 9.6, $J_{H_{exo}(7),H(4)}$ = 0.9); 3.33 (d, 1 H, H_{endo}(7), $J_{H_{endo}(7),H_{exo}(7)}$ = 9.6)	3.22 (s, 3 H, H(Me))
	48.9 (C(2))	31.3 (C(3))	45.4 (C(4))	38.7 (C(5))	48.2 (C(6))	38.7 (C(7))	40.4 (C(Me))
2b	3.99 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.41 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7)	2.87 (m, 1 H, H(4))	2.37 (dd, 1 H, H_{syn}(5), $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.1); 2.22 (d, 1 H, H_{anti}(5), $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4, $J_{H_{anti}(5),H(6)}$ = 1.7)	3.91 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.14 (dd, 1 H, H_{exo}(7), $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.2); 3.21 (dt, 1 H, H_{endo}(7), $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.1, $J_{H_{endo}(7),H(4)}$ = 1.1)	3.40 (q, 2 H, H(Et), $\underline{CH_2}CH_3$, J = 7.3); 1.28 (t, 3 H, $CH_2\underline{CH_3}$, H(Et), J = 7.3)
2c	4.15 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.4, $J_{H(2),H(3)}$ = 1.9)	4.36 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.9)	2.82 (m, 1 H, H(4))	2.37 (dd, 1 H, H_{syn}(5), $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.0); 2.15 (dd, 1 H, H_{anti}(5), $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4, $J_{H_{anti}(5),H(6)}$ = 1.9)	4.06 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.4, $J_{H(6),H_{anti}(5)}$ = 1.9)	3.04 (dd, 1 H, H_{exo}(7), $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.1); 3.13 (dt, 1 H, H_{endo}(7), $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.0, $J_{H_{endo}(7),H(4)}$ = 1.0)	7.45—7.53 (m, 5 H, H(arom.)); 4.56 (s, 2 H, H($\underline{CH_2}$Ph),)
2d	3.99 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.9)	4.26 (dt, 1 H, H(3), $J_{H(3),H(2)}$ = 1.9, $J_{H(3),H_{anti}(5)}$ = 0.6, $J_{H(3),H(4)}$ = 0.6)	2.83 (m, 1 H, H(4))	2.30 (dd, 1 H, H_{syn}(5), $J_{H_{syn}(5),H_{anti}(5)}$ = 13.5, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.3); 2.20 (dddd, 1 H, H_{anti}(5), $J_{H_{anti}(5),H_{syn}(5)}$ = 13.5, $J_{H_{anti}(5),H(6)}$ = 2.0, $J_{H_{anti}(5),H(4)}$ = 1.5, $J_{H_{anti}(5),H(3)}$ = 0.6)	3.84 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 2.0)	3.07 (dd, 1 H, H_{exo}(7), $J_{H_{exo}(7),H_{endo}(7)}$ = 9.3, $J_{H_{exo}(7),H(4)}$ = 1.1); 3.20 (ddd, 1 H, H_{endo}(7), $J_{H_{endo}(7),H_{exo}(7)}$ = 9.3, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.3, $J_{H_{endo}(7),H(4)}$ = 1.1)	3.16 (s, 3 H, H(Me))
	51.1 (C(2))	17.9 (C(3))	39.7 (C(4))	32.7 (C(5))	48.7 (C(6))	57.6 (C(7))	40.0 (C(Me))
2e	4.01 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.22 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7)	2.83 (m, 1 H, H(4))	2.29 (dd, 1 H, H_{syn}(5), $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.0); 2.15 (dd, 1 H, H_{anti}(5), $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4, $J_{H_{anti}(5),H(6)}$ = 1.7)	3.85 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.02 (dd, 1 H, H_{exo}(7), $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.0); 3.14 (dt, 1 H, H_{endo}(7), $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.0, $J_{H_{endo}(7),H(4)}$ = 1.0)	3.39 (q, 2 H, $\underline{CH_2}CH_3$, H(Et), J = 7.3); 1.27 (t, 3 H, $CH_2\underline{CH_3}$, H(Et), J = 7.3)

2f	4.25 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.6)	4.21 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.6)	2.78 (m, 1 H, H(4))	2.28 (dd, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.6, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.1); 2.10 (dd, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.6, $J_{H_{anti}(5),H(6)}$ = 1.7)	4.08 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	2.96 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.1); 3.10 (dt, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.1, $J_{H_{endo}(7),H(4)}$ = 1.1)	7.46—7.52 (m, 5 H, H(arom.)) 4.63 (s, 2 H, H($\underline{CH_2}$Ph))
2g	3.99 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.26 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7)	2.83 (m, 1 H, H(4))	2.30 (d, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.3); 2.20 (dd, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.3, $J_{H_{anti}(5),H(6)}$ = 1.7)	3.84 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.07 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.4, $J_{H_{exo}(7),H(4)}$ = 0.9); 3.20 (d, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.4)	3.16 (s, 3 H, H(Me))
2h	4.01 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.22 (d, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7)	2.83 (m, 1 H, H(4))	2.29 (d, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4); 2.15 (d, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4)	3.85 (d, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3)	3.02 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.0); 3.14 (dd, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H(4)}$ = 1.0)	3.39 (q, 2 H, $\underline{CH_2}CH_3$, H(Et), J = 7.3); 1.27 (t, 3 H, $CH_2\underline{CH_3}$, H(Et), J = 7.3)
2i	4.16 (m, 2 H, H(2), H(3))	4.16 (m, 2 H, H(2), H(3))	2.78 (m, 1 H, H(4))	2.29 (dd, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.6, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.1); 2.08 (dd, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.6, $J_{H_{anti}(5),H(6)}$ = 1.9)	4.00 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.9, $J_{H(6),H_{anti}(5)}$ = 1.9)	2.92 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.5, $J_{H_{exo}(7),H(4)}$ = 1.1); 3.03 (dt, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.5, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.1, $J_{H_{endo}(7),H(4)}$ = 1.1)	7.42—7.53 (m, 5 H, H($\underline{CH_2}$Ph, H(arom.)); 4.52 (s, 2 H, H(CH_2Ph))
2j	4.24 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.70 (t, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7, $J_{H(3),H_{anti}(5)}$ = 1.7)	2.85 (m, 1 H, H(4))	2.34 (m, 2 H, H(5))	4.10 (d, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3)	3.34 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.3, $J_{H_{exo}(7),H(4)}$ = 1.0); 3.52 (d, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.3)	3.32 (s, 3 H, H(Me))
2k	4.14 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.36 (t, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7, $J_{H(3),H_{anti}(5)}$ = 1.7)	2.80 (m, 1 H, H(4))	2.27 (dd, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.0); 2.21 (ddd, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4, $J_{H_{anti}(5),H(6)}$ = 1.7, $J_{H_{anti}(5),H(4)}$ = 1.5)	3.95 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.12 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.3, $J_{H_{exo}(7),H(4)}$ = 1.0); 3.31 (dt, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.3, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.0, $J_{H_{endo}(7),H(4)}$ = 1.0)	3.22 (s, 3 H, H(Me))
2l	4.14 (dd, 1 H, H(2), $J_{H(2),H(6)}$ = 4.3, $J_{H(2),H(3)}$ = 1.7)	4.36 (t, 1 H, H(3), $J_{H(3),H(2)}$ = 1.7, $J_{H(3),H_{anti}(5)}$ = 1.7)	2.80 (m, 1 H, H(4))	2.27 (dd, 1 H, $H_{syn}(5)$, $J_{H_{syn}(5),H_{anti}(5)}$ = 13.4, $J_{H_{syn}(5),H_{endo}(7)}$ = 1.0); 2.21 (ddd, 1 H, $H_{anti}(5)$, $J_{H_{anti}(5),H_{syn}(5)}$ = 13.4, $J_{H_{anti}(5),H(6)}$ = 1.7, $J_{H_{anti}(5),H(4)}$ = 1.5)	3.95 (dd, 1 H, H(6), $J_{H(6),H(2)}$ = 4.3, $J_{H(6),H_{anti}(5)}$ = 1.7)	3.12 (dd, 1 H, $H_{exo}(7)$, $J_{H_{exo}(7),H_{endo}(7)}$ = 9.3, $J_{H_{exo}(7),H(4)}$ = 1.0); 3.31 (dt, 1 H, $H_{endo}(7)$, $J_{H_{endo}(7),H_{exo}(7)}$ = 9.3, $J_{H_{endo}(7),H_{syn}(5)}$ = 1.0, $J_{H_{endo}(7),H(4)}$ = 1.0)	3.22 (s, 3 H, H(Me))

Table 3. ^{1}H and ^{13}C NMR spectra of compounds **4a—c**

Compound	H(2), C(2)	H(3), C(3)	H(4), C(4)	H(5), C(5)	H(6), C(6)	H(7), C(7)	H(8), C(8)	H(Me), C(Me)
4a	3.41 (dt, 1 H, H(2), $J_{H(2),H(7)}$ = 7.1, $J_{H(2),H_{syn}(3)}$ = 2.5, $J_{H(2),H_{anti}(3)}$ = 2.5)	2.04, 2.20 (both m, 1 H each, H(3))	2.42, 1.73 (both m, 1 H each, H(4))	2.60 (m, 1 H, H(5))	4.82 (t, 1 H, H(6), $J_{H(6),H(7)}$ = 4.5, $J_{H(6),H_{anti}(4)}$ = 4.5)	3.93 (dd, 1 H, H(7), $J_{H(7),H(2)}$ = 7.1, $J_{H(7),H(6)}$ = 4.5)	3.53 (dd, 1 H, $H_{exo}(8)$, $J_{H_{exo}(8),H_{endo}(8)}$ = 10.8, $J_{H_{exo}(8),H(5)}$ = 4.6); 3.69 (d, 1 H, $H_{endo}(8)$, $J_{H_{endo}(8),H_{exo}(8)}$ = 10.8)	3.15 (s, 3 H, H(Me))
	49.9 (C(2))	13.3 (C(3))	35.0 (C(4))	45.2 (C(5))	19.4 (C(6))	53.2 (C(7))	57.1 (C(8))	43.3 (C(Me))
4b	3.34 (dt, 1 H, H(2), $J_{H(2),H(7)}$ = 7.2, $J_{H(2),H_{syn}(3)}$ = 2.5, $J_{H(2),H_{anti}(3)}$ = 2.5)	1.96, 2.18 (both m, 1 H each, H(3))	2.30, 1.80 (both m, 1 H each, H(4))	2.52 (m, 1 H, H(5))	4.60 (t, 1 H, H(6), $J_{H(6),H(7)}$ = 4.3, $J_{H(6),H_{anti}(4)}$ = 4.3)	3.89 (dd, 1 H, H(7), $J_{H(7),H(2)}$ = 7.2, $J_{H(7),H(6)}$ = 4.3)	3.43 (dd, 1 H, $H_{exo}(8)$, $J_{H_{exo}(8),H_{endo}(8)}$ = 10.6, $J_{H_{exo}(8),H(5)}$ = 4.7); 3.57 (d, 1 H, $H_{endo}(8)$, $J_{H_{endo}(8),H_{exo}(8)}$ = 10.6)	3.10 (s, 3 H, H(Me))
4c	3.34 (dt, 1 H, H(2), $J_{H(2),H(7)}$ = 7.2, $J_{H(2),H_{syn}(3)}$ = 2.5, $J_{H(2),H_{anti}(3)}$ = 2.5)	1.96, 2.18 (both m, 1 H each, H(3))	2.30, 1.80 (both m, 1 H each, H(4))	2.52 (m, 1 H, H(5))	4.60 (t, 1 H, H(6), $J_{H(6),H(7)}$ = 4.3, $J_{H(6),H_{anti}(4)}$ = 4.3)	3.89 (dd, 1 H, H(7), $J_{H(7),H(2)}$ = 7.2, $J_{H(7),H(6)}$ = 4.3)	3.43 (dd, 1 H, $H_{exo}(8)$, $J_{H_{exo}(8),H_{endo}(8)}$ = 10.6, $J_{H_{exo}(8),H(5)}$ = 4.7); 3.57 (d, 1 H, $H_{endo}(8)$, $J_{H_{endo}(8),H_{exo}(8)}$ = 10.6)	3.10 (s, 3 H, H(Me))

Table 4. Physicochemical characteristics of compounds **2a—i** and **4a—c**

Compound	M.p. (°C)	Molecular formula	Found / Calculated (%)			Yield (%)
			C	H	N	
2a	117	$C_7H_{11}NBr_4$	19.83 / 19.61	2.79 / 2.59	3.00 / 3.27	100
2b	93	$C_8H_{13}NBr_4$	21.93 / 21.67	3.02 / 2.93	3.18 / 3.16	86
2c	75	$C_{13}H_{15}NBr_4$	33.59 / 30.89	3.25 / 2.97	2.64 / 2.77	80
2d	136	$C_7H_{11}NI_2Cl_2$	18.56 / 19.38	2.02 / 2.56	2.19 / 3.23	73
2e	150	$C_8H_{13}NI_2Cl_2$	21.10 / 21.43	2.77 / 2.90	2.94 / 3.13	74
2f	115	$C_{13}H_{15}NI_2Cl_2$	30.22 / 30.62	2.78 / 2.97	2.60 / 2.75	85
2g	132	$C_7H_{11}NI_2Br_2$	16.02 / 16.08	1.74 / 2.12	1.98 / 2.68	72
2h	144	$C_8H_{13}NI_2Br_2$	17.23 / 17.90	2.05 / 2.44	2.28 / 2.61	69
2i	104	$C_{13}H_{15}NI_2Br_2$	25.98 / 26.07	2.43 / 2.53	2.12 / 2.34	59
4a	130	$C_8H_{13}NBr_4$	21.72 / 21.67	2.91 / 2.93	3.14 / 3.16	100
4b	140	$C_8H_{13}NI_2Cl_2$	20.44 / 21.43	2.74 / 2.90	3.07 / 3.13	33
4c	146	$C_8H_{13}NI_2Br_2$	17.79 / 17.88	2.36 / 2.42	2.42 / 2.61	29

(760 Torr), n_D^{20} 1.4710. Found (%): C, 77.28; H, 10.82; N, 11.05. $C_8H_{13}N$. Calculated (%): C, 78.00; H, 10.64; N, 11.37.

2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene (1c) was obtained from freshly distilled cyclopentadiene (17 mL, 206 mmol), 37% formalin (12 mL, 137 mmol of formaldehyde), benzylamine

Table 5. Crystallographic parameters and a summary of data collection for compound **2d**

Parameter	Value
Molecular formula	$C_7H_{11}NI_2Cl_2$
Molecular mass	433.87
Crystal system	Monoclinic
Space group	$P2(1)/m$
a/Å	7.5817(12)
b/Å	7.9797(12)
c/Å	10.446(2)
α/deg	90.00
β/deg	96.247(3)
γ/deg	90.00
V/Å^3	628.23(18)
Z	2
d_{calc}/g cm^{-3}	Not determined
μ/cm^{-1}	5.388
Scan range ($\theta_{min}/\theta_{max}$)	3.22/28.40
Number of the measured reflections (R_{int})	1414
Number of the reflections with $I \geq 2\sigma$	1299
Number of the refined parameters	57
R_1 ($I \geq 2\sigma$)	0.0809
wR_2 (for all reflections)	0.2564

hydrochloride (20 g, 137 mmol), and water (12 mL). The reaction was carried out at ~20 °C for 3 h. The yield of compound **1c** was 17.5 g (73%), b.p. 129—131 °C (15 Torr), n_D^{20} 1.5502.

2-Methyl-2-azabicyclo[2.2.2]oct-5-ene (3) was obtained from cyclohexa-1,3-diene (27.5 mL, 275 mmol), 37% formalin (30 mL, 371 mmol of formaldehyde), and methylamine hydrochloride (25 g, 371 mmol). The reaction was carried out at 55 °C for 42 h and the product was treated as described for an excess of diene. The yield of compound **2** was 5.9 g (17%), b.p. 159—161 °C (760 Torr), n_D^{21} 1.4854 (see Ref. 11).

Bromination of azabicycloolefins (general procedure). A solution of bromine (2 equiv.) in 10 mL of CCl_4 was added dropwise to a vigorously stirred solution of an azabicycloalkene (10 mmol) in 20 mL of CCl_4 at −18 to −22 °C. After the bromine was added completely, the reaction temperature was brought to 25 °C. The orange precipitate that formed was filtered off, dried in a desiccator over NaOH, and recrystallized from ethanol. The characteristics of **3-bromo-1-methyl- (2a), 3-bromo-1-ethyl- (2b), 1-benzyl-3-bromoazoniatricyclo[2.2.1.0^{2,6}]heptane tribromides (2c),** and **6-bromo-1-methyl-1-azoniatricyclo[3.2.1.0^{2,7}]octane tribromide (4a)** are given in Table 4.

Iodination of azabicycloolefins (general procedure). Potassium dichloroiodate(I)[6] or potassium dibromoiodate(I)[7] (2 equiv.) was added in portions to a stirred ice-cooled solution of an azabicycloalkene (10 mmol) in 20 mL of anhydrous chloroform. After the reagent was added completely, the reaction mixture was stirred for an additional hour. The precipitate of the product and an inorganic salt that formed was filtered off (the filtrate was removed) and washed with acetonitrile. The resulting solution was concentrated *in vacuo*, and the product was recrystallized from EtOH. The characteristics of **3-iodo-1-methyl- (2d), 1-ethyl-3-iodo- (2e), 1-benzyl-3-iodo-1-azoniatricyclo[2.2.1.0^{2,6}]heptane dichloroiodates(I) (2f), 6-iodo-1-methyl-1-azoniatricyclo[3.2.1.0^{2,7}]octane dichloroiodate(I) (4b), 3-iodo-1-methyl- (2g), 1-ethyl-3-iodo- (2h), 1-benzyl-3-iodo-1-azoniatricyclo[2.2.1.0^{2,6}]heptane dibromoiodates(I) (2i), and 6-iodo-1-methyl-1-azoniatricyclo[3.2.1.0^{2,7}]octane dibromoiodate(I) (4c)** are given in Table 4.

Reactions of azabicyclic polyhalides with the starting olefins (general procedure). A solution of an azabicycloolefin (1 equiv.) in 5 mL of acetonitrile was added dropwise to a stirred ice-cooled solution of an azabicyclic polyhalide (5 mmol) in 10 mL of acetonitrile until the reaction mixture was decolorized. The solvent was removed *in vacuo*. When the product was obtained as an oil, it was shaken with ether (5 mL) prior to crystallization. The products were used immediately after preparation for their instability.

3-Bromo-1-methyl-1-azoniatricyclo[2.2.1.0^{2,6}]heptane bromide (2j) was obtained from compounds **2a** and **1a**. The yield was 2.70 g (100%), m.p. 128—130 °C.

3-Iodo-1-methyl-1-azoniatricyclo[2.2.1.0^{2,6}]heptane chloride (2k) was obtained from compounds **2d** and **1a**. The yield was 2.72 g (100%), m.p. 98—100 °C.

3-Iodo-1-methyl-1-azoniatricyclo[2.2.1.0^{2,6}]heptane bromide (2l) was obtained from compounds **2g** and **1a**. The yield was 3.27 g (100%), m.p. 130—132 °C.

Nucleophilic opening of the aziridine ring in 3-bromo-1-methyl-1-azoniatricyclo[2.2.1.0^{2,6}]heptane bromide (2j) with sodium methoxide in methanol. A solution of compound **1a** (1.75 g, 16 mmol) in 10 mL of methanol was added dropwise to a stirred ice-cooled suspension of tribromide **2a** (6.85 g, 16 mmol) in 20 mL of methanol. Stirring was continued until the reaction mixture was decolorized. Then a solution of sodium methoxide obtained from sodium (0.75 g, 32 mmol) and methanol (15 mL) was added dropwise while cooling the mixture with ice. The resulting solution was refluxed for 30 min. The solvent was removed *in vacuo*, and the product was extracted from the residue with ether (20 mL), and the extract was filtered. When the product was isolated as hydrochloride, a saturated solution of hydrogen chloride (10 mL) in ether was added to the filtrate. The precipitate that formed was filtered off and dried. When the product was isolated as a free base, the ether was removed, and the product was distilled *in vacuo*. The yield of **7-*syn*-bromo-6-*exo*-methoxy-2-methyl-2-azabicyclo[2.2.1]heptane (5)** was 2.10 g (30%), b.p. 135 °C (35 Torr), n_D^{16} 1.5181. ^{1}H NMR, δ: 4.06 (t, 1 H, H(7), $J_{H(7)H_{endo}(5)}$ = 1.3 Hz, $J_{H(7)H(6)}$ = 1.3 Hz); 3.62 (ddd, 1 H, H(6), $J_{H(6)H_{endo}(5)}$ = 7.5 Hz, $J_{H(6)H_{exo}(5)}$ = 3.7 Hz, $J_{H(6)H(7)}$ = 1.3 Hz); 3.31 (s, 3 H, H(MeO)); 3.15 (m, 1 H, H(1)); 2.48 (m, 3 H, H(3), H(4)); 2.40 (s, 3 H, H(MeN)); 2.03 (ddd, 1 H, H_{exo}(5), $J_{H_{exo}(5)H_{endo}(5)}$ = 13.0 Hz, $J_{H_{exo}(5)H(4)}$ = 6.8 Hz, $J_{H_{exo}(5)H(6)}$ = 3.7 Hz); 1.88 (ddd, 1 H, H_{endo}(5), $J_{H_{endo}(5)H_{exo}(5)}$ = 13.0 Hz, $J_{H_{endo}(5)H(6)}$ = 7.5 Hz, $J_{H_{endo}(5)H(7)}$ = 1.3 Hz). ^{13}C NMR, δ: 81.3 (C(1)); 66.8 (C(6)); 57.4 (C(MeO)); 56.9 (C(3)); 48.0 (C(MeN)); 43.4 (C(4)); 42.1 (C(5)); 35.5 (C(7)). The yield of **5**·HCl was 4.68 g (57%), m.p. 227 °C ($CHCl_3$/Et_2O). Found (%): C, 37.38, H, 5.96, N, 5.30. $C_8H_{14}NOBr$·HCl. Calculated (%): C, 37.45, H, 5.89, N, 5.46.

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