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Inductive Hydroxyhalogenation of Bicyclo[2.2.1]heptenes and Synthesis of Amino Alcohols from the Reaction Products

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Abstract—A method of synthesis of aminobicycloheptanols by the hydroxyhalogenation of bicyclo[2.2.1]-heptene and its alkyl derivatives in a cycloolefin–oxidant–hydrogen halide system to induce electrophilic intermediates followed by substitution of the halogen atoms by amino groups of different compositions and structures. It was found that the selectivity of the reaction depends on the formation/consumption rate ratio for the electrophilic intermediate. A high selectivity with respect to hydroxyhalides takes place, when the consumption rate of the latter intermediate is higher than its formation rate. An increase in the pH of the medium becomes higher than 10.5 decreases the yield of amino alcohols and changes the reaction direction due to acceleration of dehydrohalogenation and formation of the corresponding epoxides.

Keywords: halobicycloheptanol, aminolysis, aminobicycloheptanols, inductive addition, antimicrobial and bactericidal properties

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Aminolysis of epoxide compounds is the most convenient and widespread method of synthesis of amino alcohols. According to [1], the process can be complicated by the reaction of primary adducts with the starting epoxides. The information on the conversion of oxirane compounds with mono-, bi-, and tricyclic bridging fragments into amino alcohols has been summarized in [2–8]. However, epoxides derived from bicyclic bridged hydrocarbons, such as *exo*-3-oxotricyclo[3.2.1.$0^{2.4}$]octane and its alkyl derivatives, unlike epoxides derived from C_5–C_6 cycloolefins, are quite stable in aminolysis reactions [4]. The yield of vicinal amino alcohols here is strongly dependent on the structure of the starting compounds [2–4].

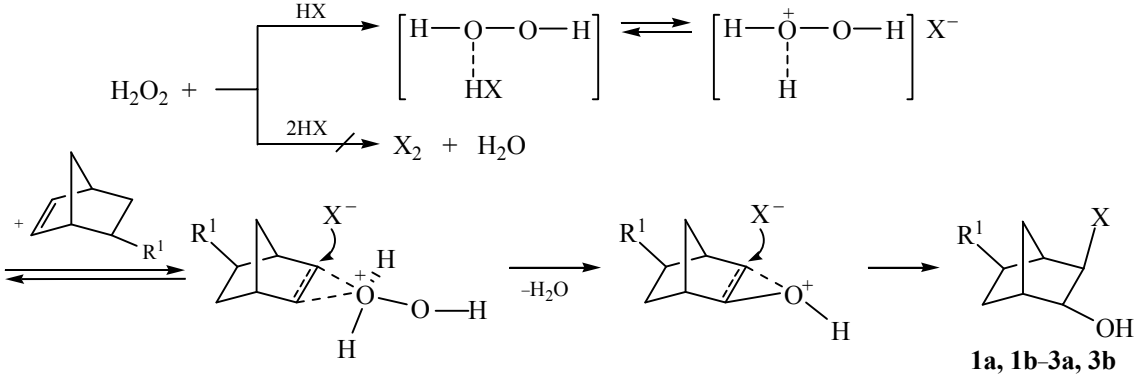
Cyclic amino alcohols are biologically active compounds, and their N- and O-derivatives are widely used in the production of pharmaceuticals [3, 9–11].

The formation of amino alcohols of the bicycloheptane series from the corresponding hydroxyhalides, unlike the situation with epoxides, is hardly controlled by steric factors. The synthesis of aminoalcohols from hydroxyhalogen derivatives of the above-mentioned hydrocarbons has almost never been reported in the literature. In this connection, the synthesis of such compounds, along with the transformation of oxiranes of different structures under the action of nitrogen-containing nucleophilic reagents, are quite important both from the theoretical and practical viewpoints.

In the present work we report the results of our research on the synthesis of hydroxyhalides of bicyclo-[2.2.1]hept-2-ene and its alkyl derivatives by in situ addition of the electrophilic intermediates formed in the HX–H_2O_2–cycloolefin system, as well as the synthesis of amino alcohols from the resulting hydroxyhalides. We also studied the effect of substituents on the antimicrobial and bactericide properties of the synthesized amino alcohols included in the compositions of lubricant oils and lubricant cutting fluid.

We previously showed [12, 13] that electrophilic reagents HOX (X = Cl, Br) selectively add *in situ* across the multiple bonds in substrates. It was found that bicyclo[2.2.1]hept-2-ene and its alkyl derivatives in mild conditions (30–50°C) take up the electrophilic intermediates formed from the H_2O_2–HX mixture (X = Cl, 10–15%; X = Br, 8–10% aqueous solution) in the

Scheme 1.



X = Cl (**a**), Br (**b**); R = H (**1**), 5-CH_3 (**2**), 5-CH=CH_2 (**3**).

course of the reaction to form hydroxychlorides **1a**–**3a** and hydroxybromides **1b**–**3b** (Scheme 1).

In situ hydroxyhalogenation of the substrates involves the electrophilic oxygen formed in the aqueous phase in the reaction of H_2O_2 and HX. Since in the steady-state system this intermediate is present in the aqueous phase, its addition across the double bond of the substrate takes place at the phase interface. To drive the reaction, more vigorous stirring of the reaction mixture should be applied. The yields of products **1**–**3** are strongly dependent on the reaction temperature, concentrations of the aqueous solutions of HX and H_2O_2, and molar ratio of the components. The addition of the electrophilic intermediate to the double bond competes with its unproductive decomposition. Consequently, the optimal parameters of the process should be varied so that the rate of addition of the electrophilic intermediate is higher than its formation and unproductive decomposition rates. In this case, high yields of and selectivity with respect to reactions products **1**–**3** can be achieved.

In the absence of an oxidant, no hydroxyhalogenation of cycloolefins takes place, because hydrogen halide in a dilute aqueous solution does not undergo inductive oxidation to form an intermediate containing an electrophilic oxygen atom.

The highest yields of compounds **1a**–**3a** (65–72.5%) and **1**–**3** (61–69%) were obtained at the substrate : HX : H_2O_2 molar ratio of 1 : 1 : 1.5 with 10–15 and 8–10% aqueous HCl and HBr, respectively. With less concentrated HCl and HBr solutions (6–10% and 5–8%, respectively), worse results were obtained.

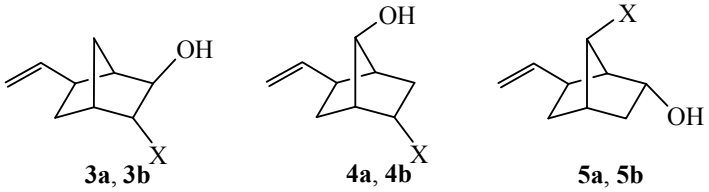
In the range 30–60°C, the yields of hydroxyhalogenation products increase with increasing temperature to reach 62–76.5% (**1a**–**3a**) and 58–71.6% (**1b**–**3b**) at 50–55°C. It should be noted that to increase the temperature above 55°C is inexpedient, because this accelerates the unproductive decomposition of the electrophilic intermediate to form molecular chlorine (or bromine) and accumulation in the oxidate of their addition products across the double bond, specifically, dihalo derivatives of the bicyclic hydrocarbons (up to ~15–25%).

According to the GLC, IR, and ^{1}H and ^{13}C NMR data, increased temperature induces rearrangement of the functional groups. Thus, in the hydroxyhalogenation of 5-ethenylbicyclo[2.2.1]hept-2-ene, along with the main isomer of 5-ethenyl-*exo*, *endo*-2(3)-halobicyclo[2.2.1]heptan-3(2)-ol **3a**, **3b** (89–92%), we also detected among the reaction products (up to 2–6%) 5-ethenyl-*endo,endo*-2(3)-halobicyclo[2.2.1]heptan-3(2)-ol, 5-ethenyl-*exo,endo*-2(3)-halobicyclo[2.2.1]heptan-3(2)-ol, 5-ethenyl-*endo(syn)*-3(7)-halobicyclo[2.2.1]-heptan-7(3)-ol (**4a**, **4b**), and 5-ethenyl-*endo(syn)*-7(2)-halobicyclo[2.2.1]heptan-2(7)-ol (**5a**, **5b**) (Scheme 2).

The presence in the hydroxyhalogenation products of small amounts (2–6%) of isomers **4a**, **4b** and **5a**, **5b** provides evidence showing that hydroxyhalogenation of bicyclo[2.2.1]hept-2-ene derivatives may be accompanied by the Wagner–Meerwein rearrangement.

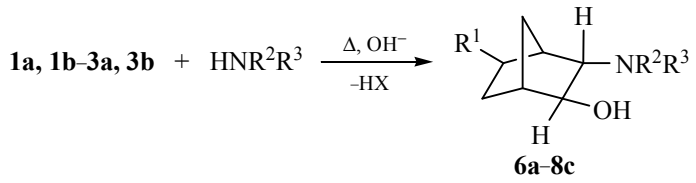
The ^{1}H and ^{13}C NMR spectra of the mixture of 5-ethenylbromobicyclo[2.2.1]heptanol isomers display, along with the absorption bands of the main isomer 5-ethenyl-*exo*(*endo*)-2(3)-bromobicyclo[2.2.1]heptan-*endo*(*exo*)-3(2)-ol **3b**, unresolved signals which we assigned to isomers **4b** and **5b** [3.87 (1H, HCOH), 3.68 (1H, HCOH), 3.46 (1H, HCBr), 3.41 (1H, CHBr), and 4.96–5.95 ppm (3H,–CH=CH_2)]. The carbon atoms bearing the OH group and bromine atom give

Scheme 2.



3a, **3b** **4a**, **4b** **5a**, **5b**

Scheme 3.



6a–**8c**

R^1 = H (**6a**–**6c**), 5-CH_3 (**7a**–**7c**), CH_2=CH (**8a**–**8c**); R^2, R^3 = $(–CH_2–)_5$ (**a**), $(–CH_2CH_2)_2O$ (**b**), R^2 = H, R^3 = C_6H_5 (**c**).

^{13}C NMR signals at 75 (**4b**), 73 (**5b**), and 49.5 ppm (**4b**, **5b**).

The synthesized chloro(bromo)bicyclo[2.2.1]heptanols **1**–**3** were used to obtain N-substituted amino alcohols **6**–**8** (Scheme 3).

The transformation direction of hydroxychloro (bromo) derivatives and the yield of N-substituted bicyclo[2.2.1]heptanols are primarily dependent of the reaction temperature, pH of the medium, and nature and polarity of the solvents.

To find out the effect of different parameters on the substitution of halogens in chloro(bromo)hydroxybicycloheptanes by amines, we chose as the model reaction the reaction of 3-bromobicyclo[2.2.1]heptan-2-ol with piperidine. It was found that an increase of the temperature in the range 20–60°C increases the yield of piperidinylbicyclo-[2.2.1]heptanol and also decreases the reaction time from 12 to 3.5 h. Changing the pH and polarity of the medium affects not only the yield of the target reaction product, but also the very possibility of this reaction. Thus, for example, anhydrous reagents fail to react at all, whereas the presence of water or alcohols [C_2H_5OH, $CH_3CH(OH)CH_3$] substantially accelerate the reaction. When the pH of the medium is increased from 8.2 to 10.2, the reaction efficiently occurs at 40–60°C, whereas at pHs higher than 10.5 the reaction changes direction. In this case, the formation of the corresponding amino alcohol is accompanied by acceleration of the dehydrobromination of the starting hydroxybromobicycloheptane **1b** into the corresponding oxirane. The reaction yield is also affected by the ratio of the starting reagents. A high yield is reached with an excess of the starting piperidine (1.5–2.5), which completely excludes condensation of the resulting amino alcohols with elimination of a water molecule (Table 1).

It should also be noted that in each concrete case the yield of each concrete amino alcohol from the corresponding bromobicyclo[2.2.1]heptanol is 5–8% higher than from its chlorine-containing analog. This result is probably explained by easier substitution of bromine in hydroxybromides compared to chlorine in hydroxychlorides. The yields and spectral characteristics of the synthesized amino alcohols are given in Experimental.

The obtained N-substituted bicyclo[2.2.1]heptanols were tested as antimicrobial additives to motor oils M8, M10 [12] and emulsion lubricant cutting fluid Azerol-5. According to the testing results, some representatives of this class of compounds in concentrations of 0.25–1.00% showed activity and protective properties (Table 2). The activity of the tested compounds in the lubricant cutting fluid was higher than in lubricant oils, probably, due to their higher solubility in the fluid. The bactericide and fungicide activity of the compounds is also dependent of the structure and composition of the substituents on the nitrogen atom (Table 2).

EXPERIMENTAL

The primary and secondary amines, H_2O_2, HCl, and HBr were purached from Alfa Aesar (div. of Johnson

Table 1. Effect of reaction conditions of 3-bromobicyclo[2.2.1]heptan-2-ol and piperidine on the yield of 3-(piperidin-1-yl)-bicyclo [2.2.1]heptan-2-ol

T, °C	Reaction time, h	Solvent	Amine: bromobicyclo[2.2.1]heptan-2-ol ratio	pH	Yield, %
20	12	–	1.5 : 1	9.8	0.0
30	10	H_2O	1.5 : 1	9.8	15.0
40	8.0	$CH_3CH(OH)CH_3$–H_2O	1.5 : 1	8.2	56.0
50	5.0	C_2H_5OH–H_2O	1.5 : 1	9.8	63.0
60	4.0	$CH_3CH(OH)CH_3$–H_2O	1.5 : 1	10.0	67.0
50	5.0	$CH_3CH(OH)CH_3$–H_2O	2.0 : 1	10.2	69.0
60	3.0	$CH_3CH(OH)CH_3$–H_2O	2.0 : 1	10.2	73.0
50	4.5	$CH_3CH(OH)CH_3$–H_2O	2.5 : 1	10.2	73.5
60	3.5	C_2H_5OH–H_2O	2.5 : 1	10.2	75.0

Malthey). The starting bicyclo[2.2.1]hept-2-enes were synthesis by the [4+2] addition of cyclopentadiene (cyclopentadiene dimer monomerization conditions can also be applied) to C_2–C_4 olefins in the presence of the H forms of clinoptilolite (SiO_2/Al_2O_3 = 5.4) or mordenite (SiO_2/Al_2O_3 = 10) by a known procedure [14].

The IR spectra were measured on an Alpha FTIR spectrometer in the range 400–4000 cm^{-1} for KBr pellets. The ^1H and ^{13}C NMR spectra were run on a Bruker BioSpin AG spectrometer at 300.18 MHz in $CDCl_3$. Elemental analysis were performed on a LECO TruSpes Micro analyzer.

Hydroxychlor(brom)ination of bicyclo[2.2.1]hept-2-enes *(general procedure).* Hydroxychlor(brom) ination of bicyclo[2.2.1]hept-2-ene and its derivatives was performed by the procedure described in [12, 13]. Hydrogen peroxide, 0.2–0.25 mol of a 26–30% aqueous solution, was added at a rate of 10 g/h to a vigorously stirred (250–300 rpm) mixture of 8–15% HCl or HBr (0.15–0.2 mol) and 0.1 mol of bicycloheptene or its derivative. The mixture was stirred for 5–6 h. The reaction was complete after all oxidant had been consumed (control be permanganometric or iodometric titration [15]). The organic layer was then separated, and the aqueous layer was extracted with diethyl ether or toluene (2×100 mL). The extracts were combined with the organic layer, neutralized with 10% aqueous Na_2CO_3, dried with $MgSO_4$, and the solvent was removed by distillation to isolate products **1a**–**3a** or **1b**–**3b**.

Synthesis of amino alcohols from hydroxychloro-(bromo) derivatives of bicyclo[2.2.1]heptanes *(general procedure).* Propan-2-ol, 50–100 mL, and 0.3 g of KOH were added to 14.7 g (0.1 mol) of compound **2a** or 19.1 g of compound **3a**, isolated from the catalyzate. The mixture was heated for 1–1.5 h at 40–60°C, and then 0.2–0.25 mol of primary or secondary amine was added to it dropwise over the course of 0.5–1.0 h under stirring. The reaction occurred for 3–6 h until hydroxyhalide was consumed completely (control be GLC). The solvent was then removed, and the mixture was cooled down to obtain the target products **6**–**8**.

3-Chloro-5-ethenylbicyclo[2.2.1]heptan-2-ol (3a) was obtained from 6.0 g (50 mmol) of 5-ethenylbicyclo[2.2.1]hept-2-ene. Yield 5.4 g (62.6%), bp 102–104°C (2.5 mmHg). IR spectrum, ν, cm^{-1}: 3485, 3360 (OH), 3080, 3050 (CH_2=), 1640 (C=C), 1460 (CH_2), 1125, 1095 [δ(OH)], 780, 760 (C–Cl) [16]. ^1H NMR spectrum, δ, ppm: 1.32–2.18 m (7H, $2CH_2$ + 3CH), 3.45 t (1H, HCOH, *J* = 7.2 Hz), 3.52 t (1H, HC–Cl, *J* = 7.3 Hz), 3.61 br.s (1H, OH), 4.11 d.d (1H, H^aH^bC=CH, *J* = 10.3, 2.3 Hz), 5.1 d.d (1H, H^aH^bC=CH, *J* = 16.8, 2.2 Hz), 5.82 d.d.d (1H, HC=CH_2, *J* = 16.7, 10.3, 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 142 (C^8), 114 (C^9), 78 (C^2), 66.5 (C^3), 39 (C^5), 37.5 (C^4), 36.5 (C^1), 31.8 (C^6), 29.1 (C^7) [17]. Found, %: C 62.84; H 7.49; Cl 20.41. $C_9H_{13}ClO$. Calculated, %: C 62.6; H 7.53; Cl 20.58.

3-Bromo-5-ethenylbicyclo[2.2.1]heptan-2-ol (3b) was obtained from 6.0 g (50 mmol) of 5-ethenylbicyclo[2.2.1]hept-2-ene. Yield 7.1 g (65%), bp 117–119°C (2 mmHg). IR spectrum, ν, cm^{-1}: 3492, 3350 (OH), 3080, 3050 (CH_2=), 1645 (C=C), 1460 (CH_2),

Table 2. Antimicrobial properties of some synthesized N-substituted bicycloheptanols

Comp. no.	*c*, wt %	Diameter of the growth inhibition zone, cm			
		oil -8		Azerol-5	
		mixture of bacteria	mixture of fungi	mixture of bacteria	mixture of fungi
7a	1.0	2.2–2.4	+ +	2.4–2.6	+ +
	0.5	1.8–2.0	+ +	1.–2.2	+ +
	0.25	1.6–1.4	+ +	1.6–1.4	+ +
7b	1.0	1.0–1.2	1.6–1.8	1.4–1.2	1.8–2.0
	0.5	+ +	1.2–1.4	1.2–1.2	1.6–1.8
	0.25	+ +	1.0–1.0	+ +	1.2–1.2
7c	1.0	1.0–1.2	1.2–1.2	+ +	1.2–1.4
	0.5	+ +	0.9–1.9	+ +	+ +
	0.25	+ +	+ +	+ +	+ +
8a	1.0	2.3–2.5	+ +	2.5–2.7	+ +
	0.5	1.9–2.1	+ +	1.9–2.3	+ +
	0.25	1.6–1.4	+ +	1.6–1.3	+ +
8b	1.0	1.1–1.3	1.8–2.0	1.6–1.4	1.6–1.8
	0.5	+ +	1.6–1.8	1.2–1.2	1.4–1.6
	0.25	+ +	1.8–1.2	+ +	1.1–1.1
8c	1.0	1.1–1.3	1.3–1.3	+ +	1.3–1.5
	0.5	1.0–0.8	0.8–1.8	+ +	+ +
	0.25	+ +	+ +	+ +	+ +
8-Oxoquinoline	1.0	0.8–1.0	1.4		
	0.5	0.5–0.7			
Sodium pentachlorophenolate	1.0	1.1–1.3	1.4–1.4		
	0.5	0.7–1.0	0.8–1.2		
Oil M-8 (neat)	–	+ +	+ +		
Azerol-5				+ +	+ +

1125, 1085 [δ(OH)], 550–610 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.33–2.19 m (7H, $2CH_2$ + 3CH), 3.49 t (1H, HCBr, *J* = 7.3 Hz), 3.62 t (1H, HCOH, *J* = 7.2 Hz), 3.73 br.s (1H, OH), 4.95 d.d (1H, H^aH^bC=CH, *J* = 10.3, 2.3 Hz), 5.1 d.d (1H, H^aH^bC=CH, *J* = 16.8, 2.2 Hz), 5.83 d.d.d (1H, HC=CH_2, *J* = 16.7, 10.3, 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 149 (C^8), 114.8 (C^9), 78.5 (C^2), 61.0 (C^3), 40.5 (C^4), 38.6 (C^4), 37.5 (C^5), 31.1 (C^6), 30.4 (C^7)]. Found, %: C 49.68; H6.15; Br 36.87. $C_9H_{13}BrO$. Calculated, %: C 49.77; H 5.99; Br 36.87.

3-(Piperidin-1-yl)bicyclo[2.2.1]heptan-2-ol (6a) was obtained from 4.4 g (30 mmol) of compound **1a** or 5.73 g (30 mmol) of compound **1b** and 5.1 g (60 mmol) of piperidine. Yield 3.8 g (64.8%, **1a**), 4.1 g (70.1%, **1b**), mp 83–85°C. IR spectrum, ν, cm^{-1}: 3480 (OH), 3250 (CN), 2860–2865 (CH_2), 1535 (CN), 1470–1465 [$\delta_{as}(CH_2)$], 1360 [δ(CH)], 1295 (N–C), 1080 [δ(OH)]. ^{1}H NMR spectrum, δ, ppm: 1.36–2.21 m (16H, CH_2 + CH), 2.44 t [4H, $(CH_2)_2$N, *J* = 7.2 Hz], 2.62 t [1H, HCN$(CH_2)_2$, *J* = 6.9 Hz], 3.4 t (1H, H^2, 7.1 Hz), 3.61 br.s (1H, OH). Found, %: C 73.49; H 10.85; N 6.95. $C_{12}H_{21}NO$. Calculated, %: C 73.85; H 10.77; N 7.18.

3-(Morpholin-4-yl)bicyclo[2.2.1]heptan-2-ol (6b) was obtained from 4.4 g (30 mmol) of compound **1a** or 5.73 g (30 mmol) of compound **1b** and 5.22 g (60 mmol) of morpholine. Yield 4.0 g (67.3%, **1a**), 4.4 g (74.1%, **4b**), mp 96–98°C. IR spectrum, ν, cm^{-1}: 3482 (OH), 3321 (CN), 2860–2855 (CH_2), 1521 (CN), 1296 (N–C), 1250 (C–O–C), 1112 [δ(OH)], 870, 854. ^{1}H NMR spectrum, δ, ppm: 1.35–2.16 m (8H, CH_2 + CH), 2.68 t [2H, $(CH_2)_2$N, *J* = 7.3 Hz], 3.41 t (1H, H^2, *J* = 6.9 Hz), 3.56 br.s (1H, OH), 3.61 t [4H, $(CH_2)_2$O,

J = 7.2 Hz]. Found, %: C 66.76; H 9.82; N 6.94. $C_{11}H_{19}NO_2$. Calculated, %: C 67.0; H 9.64; N 7.11.

3-(Phenylamino)bicyclo[2.2.1]heptan-2-ol (6c) was obtained from 4.4 g (30 mmol) compound **1a** or 5.73 g (30 mmol) compound **1b** and 5.6 g (60 mmol) of phenylamine. Yield 4.0 g (65.6%, **1a**), 4.2 g (69%, **1b**), mp 125–127°C. IR spectrum, ν, cm^{-1}: 3450 (OH), 3435, 3320 (NH), 3250 (CN), 1660 (NH), 1640 (C=C), 1534 (CN), 1360 [δ(CH)], 1295 (CN), 1108 [δ(OH)], 778, 685 [δ(C_6H_5)]. ^{1}H NMR spectrum, δ, ppm: 1.36–2.18 m (8H, CH_2, CH), 2.67 t (1H, H^3, J = 6.9 Hz), 3.42 t (1H, H^2, J = 7.1 Hz), 3.61 br.s (1H, OH), 4.1 s (1H, N<u>H</u>C_6H_5), 6.78–6.85 m (3H, H^1, H^4, H^6, C_6H_5), 7.25l d.d (2H, H^3, H^5, C_6H_5, J = 7.5, 1.8 Hz). Found, %: C 76.55; H 8.55; N 6.57. $C_{13}H_{17}NO$. Calculated, %: C 76.85; H 8.37; N 6.89.

6-Methyl-3-(piperidin-1-yl)bicyclo[2.2.1]heptan-2-ol (7a) was obtained from 4.82 g (30 mmol) of compound **2a** or 6.15 g (30 mmol) of compound **2b** and 5.1 g (60 mmol) of piperidine. Yield 4.0 g (63.8%, **2a**), 4.5 g (71.8%, **2b**), mp 85-–87°C. IR spectrum, ν, cm^{-1}: 3478 (OH), 3250 (CN), 2958 (CH_3), 2865–2860 (CH_2), 1535 (CN), 1472–1465 [$\delta_{as}(CH_2)$], 1360 [δ(CH)], 1295 (N–C), 1085 [δ(OH)]. ^{1}H NMR spectrum, δ, ppm: 0.98 d (3H, CH_3, J = 6.7 Hz), 1.22–2.17 m (13H, CH_2, CH), 2.43 t [2H, $N(CH_2)_2$, J = 7.2 Hz], 2.67 t (1H, H^3, J = 7.0 Hz), 3.42 t (1H, H^2, J = 7.1 Hz), 3.61 br.s (1H, OH). Found, %: C 74.57; H 11.09; N 6.68. $C_{13}H_{23}NO$. Calculated, %: C 74.64; H 11.0; N 6.69.

6-Methyl-3-(morpholin-4-yl)bicyclo[2.2.1]heptan-2-ol (7b) was obtained from 4.82 g (30 mmol) of compound **2a** or 6.15 g (30 mmol) of compound **2b** and 5.22 g (60 mmol) morpholine. Yield 4.1 g (64.8%, **2a**), 4.7 g (74.2%, **2b**), mp 103–105°C. IR spectrum, ν, cm^{-1}: 3480, 3360 (OH), 3320 (CN), 2960 (CH_3), 2898 (CH_2), 2860–2855 (CH_2), 1520 (CN), 1295 (N–C), 1250 (C–O–C), 1100 [δ(OH)], 870, 854. ^{1}H NMR spectrum, δ, ppm: 0.98 d (3H, Me, J = 6.9 Hz), 1.25–2.15 m (7H, CH_2 + CH), 2.62 t (1H, H^3, J = 7.0 Hz), 2.68 t [2H, $N(CH_2)_2$, J = 7.2 Hz], 3.43 t (1H, H^2, J = 7.2 Hz), 3.56 br.s (1H, OH), 3.62 t [2H, $O(CH_2)_2$, J = 6.9 Hz]. Found, %: C 68.03; H 10.16; N 6.52. $C_{12}H_{21}NO_2$. Calculated, %: C 68.25; H 9.95; N 6.64.

6-Methyl-3-(phenylamino)bicyclo[2.2.1]heptan-2-ol (7c) was obtained from 4.82 g (30 mmol) of compound **2a** or 6.15 g (30 mmol) of compound **2b** and 5.6 g (60 mmol) of phenylamine. Yield 3.8 g (58.3%, **2a**), 4.7 g (72.2%, **2b**), mp 76–78°C (3 mmHg). IR spectrum, ν, cm^{-1}: 3485 (OH), 3436, 3320 (NH), 3250 (CN), 2959 (CH_3), 2868 (CH_2), 1660 (NH), 1640 (C=C), 1534 (CN), 1458 [$\delta_{as}(CH_3)$], 1360 [δ(CH)], 1295 (CN), 1100 [δ(OH)], 778, 685 [δ(C_6H_5)]. ^{1}H NMR spectrum, δ, ppm: 0.98 d (3H, CH_3, J = 6.7 Hz), 1.22–2.15 m (7H, CH_2, CH), 2.62 d (1H, H^3, J = 7.1 Hz), 3.41 t (1H, H^2, J = 7.2 Hz), 3.60 br.s (1H, OH), 4.1 s (1H, N<u>H</u>C_6H_5), 6.78–6.84 m (3H, H^1, H^4, H^6, C_6H_5), 7.26 d.d (2H, H^3, H^5, C_6H_5, J = 7.5, 1.7 Hz). Found, %: C 77.14; H 8.43; N 6.22. $C_{14}H_{19}NO$. Calculated, %: C 77.42; H 8.76; N 6.45.

6-Ethenyl-3-(piperidin-1-yl)bicyclo[2.2.1]heptan-2-ol (8a) was obtained from 5.2 g (30 mmol) of compound **3a** or 6.51 g (30 mmol) of compound **3b** and 5.1 g (60 mmol) of piperidine. Yield 4.2 g (63%, **3a**), 4.5 g (67.9%, **3b**), mp 98–101°C. IR spectrum, ν, cm^{-1}: 3486 (OH), 3270 (CN), 3060 (CH_2=), 3032, 3020 (CH=), 1633 (C=C), 1524 (CN), 1470 [$\delta_{as}(CH_2)$], 1365, 1348 [δ(CH)], 1246 (NC), 1105 [δ(OH)]. ^{1}H NMR spectrum, δ, ppm: 1.34–2.21 m (13H, CH_2 + CH), 2.48 t [2H, $N(CH_2)_2$, J = 7.3 Hz], 2.71 t (1H, H^3, J = 7.3 Hz), 3.42 t (1H, H^2, J = 6.7 Hz), 3.61 br.s (H, OH), 4.96 d.d (1H, C<u>H</u>^{a}H^b=CH, J = 10.3, 2.3 Hz), 5.12 d.d (1H, CH^a<u>H</u>^{b}=CH, J = 16.8, 2.2 Hz), 5.82 d.d (1H, C<u>H</u>=CH^{a}H^b, J = 16.7, 6.4 Hz). Found, %: C 75.80; H 10.25; N 6.41. $C_{14}H_{23}NO$. Calculated, %: C 76.02; H 10.40; N 6.33.

6-Ethenyl-3-(morpholin-4-yl)bicyclo[2.2.1]heptan-2-ol (8b) was obtained from 5.2 g (30 mmol) of compound **3a** or 6.51 g (30 mmol) of compound **3b** and 5.2 g (60 mmol) of morpholine. Yield 4.6 g (68.5%, **3a**), 5.0 g (74.8%, **3b**), mp 114–116.5°C. IR spectrum, ν, cm^{-1}: 3456 (OH), 3060 (CH_2=), 3035, 3020 (CH=), 1630 (C=C), 1565 (CN), 1295 (NC), 1250, 1175 (C–O–C), 1100 [δ(OH)], 942, 910, 880 (CH=CH_2). ^{1}H NMR spectrum, δ, ppm: 1.26–2.16 m (7H, CH_2 + CH), 2.66 t (1H, H^3, J = 7.2 Hz), 2.71 d [2H, $(CH_2)_2$N, J = 7.2 Hz], 3.42 t (1H, H^2, J = 6.8 Hz), 3.58 br.s (1H, OH), 3.63 d [2H, $(CH_2)_2$O, J = 7.3 Hz], 4.96 d.d (1H, C<u>H</u>^{a}H^b=CH, J = 10.2, 2.3 Hz), 4.01 d.d (1H, CH^a<u>H</u>^{b}=CH, J = 16.8, 2.2 Hz), 5.81 d.d (1H, C<u>H</u>=CH^{a}H^b, J = 16.7, 6.3 Hz). Found, %: C 69.79; H 8.89; N 6.16. $C_{13}H_{21}NO_2$. Calculated, %: C 69.96; H 9.42; N 6.3.

6-Ethenyl-3-(phenylamino)bicyclo[2.2.1]heptan-2-ol (8c) was obtained from 5.2 g (30 mmol) of compound **3a** or 6.51 g (30 mmol) of compound **3b** and 5.6 g (60 mmol) of phenylamine. Yield 3.8 g (55.1%, **3a**), 4.2 g (61.2%, **3b**), mp 76–78°C

(3.5 mmHg). IR spectrum, ν, cm^{-1}: 3483 (OH), 3320 (NH), 3060 (CH=), 3250 (CN), 2959 (CH_3), 2868 (CH_3), 1665 (NH), 1636 (C=C), 1525 (CN), 1465 [$\delta_{as}(CH_2)$], 1345 [δ(CH)], 1295 (CN), 1100 [δ(OH)], 776–685 [$\delta(C_6H_5)$]. ^{1}H NMR spectrum, δ, ppm: 1.29–2.18 m (7H, CH_2 + CH), 2.68 d (1H, H^3, J = 7.1 Hz), 3.42 t (1H, H^2, J = 6.9 Hz), 3.61 br.s (H, OH), 4.1 s (1H, N<u>H</u>C_6H_5), 4.92 d.d (1H, C<u>H</u>^{a}H^b=CH, J = 10.2, 2.3 Hz), 5.04 d.d (1H, CH^a<u>H</u>^{b}=CH, J = 16.8, 2.1 Hz), 5.82 d.d (1H, C<u>H</u>=CH^{a}H^b, J = 16.7, 6.3 Hz), 6.78–6.85 m (3H, H^1, H^4, H^6, C_6H_5), 7.25 d.d (2H, H^3, H^5, C_6H_5, J = 7.5, 1.8 Hz). Found, %: C 77.86; H 8.36; N 5.91. $C_{15}H_{19}NO$. Calculated, %: C 78.60; H 8.29; N 6.11.

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