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Synthesis and Epoxidation of 5-(2-Aminoethyl)bicyclo[2.2.1]hept-2-ene Derivatives

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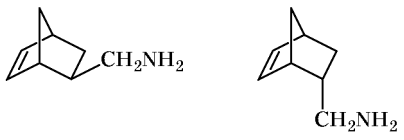
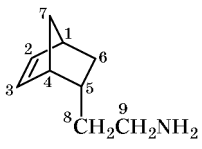
Abstract—A number of derivatives of 5-(2-aminoethyl)bicyclo[2.2.1]hept-2-ene (85–90% of the *endo* isomer) were synthesized by reactions with *p*-nitrobenzenesulfonyl chloride, *p*-toluenesulfonyl chloride, benzoyl chloride, *p*-nitrobenzoyl chloride, benzyl isocyanate, *m*-tolyl isocyanate, phenyl isothiocyanate, and endic anhydride. By reactions of the resulting sulfon- and carboxamides with peroxyphthalic acid generated *in situ* from phthalic anhydride and 40–45% hydrogen peroxide the corresponding epoxy derivatives were obtained. These reactions were not accompanied by heterocyclization into azabrendane derivatives, which is typical of homologous *N*-(*p*-nitrophenylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene.

Pharmacophoric norbornene fragment, as well as related norbornane and adamantane moeities, acquires a specific importance in molecules of amines, many of which are used as medicines [1]. Among amines containing a norbornene fragment, the most widely known and extensively studied are stereoisomeric *exo*- and *endo*-5-aminomethylbicyclo[2.2.1]hept-2-enes **Ia** and **Ib** (Scheme 1).

Scheme 1.



Ia **Ib**



II

In the recent years various derivatives of amines **Ia** and **Ib** were synthesized, such as sulfonamides [2], carboxamides [3], urea and thiourea derivatives [4], and products of reactions with endic, naphthalic, and substituted naphthalic anhydrides [5, 6]. The spectral parameters [7] and biological activity of these compounds were studied [8]. It was found that orientation of the substituent in the norbornene fragment affects both spectral parameters and chemical behavior of amine derivatives in reactions with peroxy acids. Stereochemical features of sulfonamides derived from amines **Ia** and **Ib** determine both the kind and the strength of neurotropic (analgetic, anticonvulsant, antihypoxic, tranquilizing) and antiphlogistic activity.

Homologs of amines **Ia** and **Ib** were studied very poorly. A saturated analog of **II** was used as starting compound for preparation of adenosine A_2 receptor agonists [9]. We expected that variation of the length of the hydrocarbon chain connecting the amino group and the bicyclic skeleton should give rise to new biologically active substances. This assumption was based, in particular, on the new data on biological activity of adamantane amino derivatives: separation of the amino group from the adamantane core by 2–3 methylene units leads to increase of antiviral activity [10].

In the present work we synthesized derivatives of amine **II** and studied their reactions with peroxyphthalic acid. Amine **II** was synthesized from the Diels–Alder adduct of cyclopentadiene and acrolein, which was obtained under mild conditions of kinetic control. The major product was the corresponding *endo* isomer (**III**) [11] (Scheme 2). Amine **II** was synthesized from aldehyde **III** by modified procedure [12] via condensation with nitromethane in alkaline medium, followed by reduction of unsaturated nitro compound **IV** with lithium aluminum hydride.

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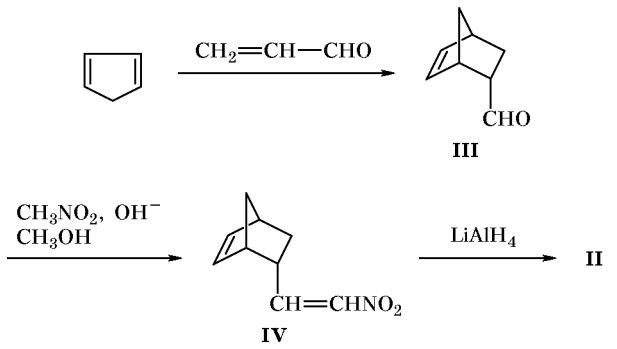
The reduction occurred chemoselectively, involving two of the three possible centers, and target product **II** was obtained in 65–70% yield.

Scheme 2.

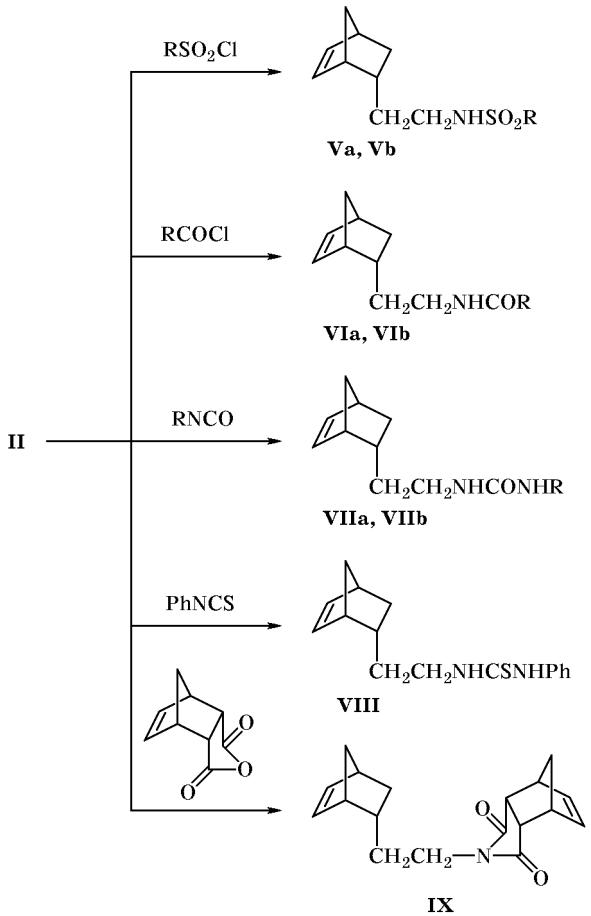


Amine **II** was brought into reactions with a number of electrophilic reagents: *p*-nitrobenzenesulfonyl chloride, *p*-toluenesulfonyl chloride, *p*-nitrobenzoyl chloride, benzoyl chloride, benzyl isocyanate, *m*-tolyl isocyanate, phenyl isothiocyanate, and endic anhydride (Scheme 3). Sulfonamides **Va** and **Vb** were obtained in the two-phase system diethyl ether–20% aqueous sodium hydroxide; carboxamides **VIa** and **VIb** were synthesized in chloroform in the presence of pyridine, and the other reactions were carried out in benzene. The reaction with endic anhydride under such mild conditions usually leads to formation of amido acids [5]; however, from amine **II** we obtained imide **IX**. The yields, melting points, IR spectra, and elemental analyses of products **V**–**IX** are given in Table 1.

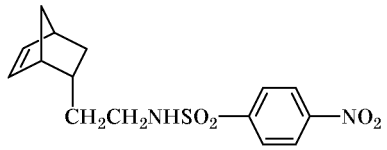
The IR spectra of amides **VIa** and **VIb** and ureas **VIIa** and **VIIb** characteristically contain amide absorption bands in the regions 1640–1630 (ν C=O), 1570–1550 (δ N–H), and 1270–1250 cm^{-1} (ν C–N). The IR spectrum of thiourea **VIII** lacks amide I band but displays absorption at 1330 cm^{-1} which was assigned to stretching vibrations of the C=S group. Sulfonamides **Va** and **Vb** clearly show in the IR spectra absorption bands due to SO_2 group at 1360–1340 and 1175–1155 cm^{-1} [13]. The nitro group in molecules **Va** and **VIa** gives rise to absorption bands at 1545–1520 and 1350–1330 cm^{-1}, typical of its symmetric and antisymmetric vibrations. All amine **II** derivatives show in the IR spectra absorption at 3400–3200 cm^{-1} due to stretching vibrations of the N–H bond; the spectra of **VIIa**, **VIIb**, and **VIII** are characterized by the presence of two bands in that region, whereas no ν N–H band is observed in the spectrum of imide **IX**. The latter gives a weak absorption at 1581 cm^{-1} due to stretching vibrations of double carbon–carbon bonds in the two bicyclic fragments. The corresponding band in the IR spectra of the other compounds is obscured by absorption of the amino group (δ NH) and aromatic fragments [14]. Imide **IX** is also characterized by the presence in the IR spectrum of two carbonyl bands at 1750 and 1700 cm^{-1} and a band at 3070–3060 cm^{-1} which belongs to stretching vibrations of olefinic =C–H bonds in the norbornene fragments. Analogous bands in the spectra of the other derivatives are overlapped by absorption of aromatic C–H bonds. Bending vibrations of the H–C= bonds in **IX** appear at 730 cm^{-1}.

Table 2 contains the ^{1}H NMR spectra of compounds **Ib**, **II**, **Va**, **VIa**, **VIIa**; for comparison, the ^{1}H NMR spectrum of previously described biologically active sulfonamide **X** [15] is also given. Apart from some similarity, the ^{1}H NMR spectra of derivatives of amines **II** and **Ib** have considerable differences. The predominant *endo* orientation of the 5-substituent

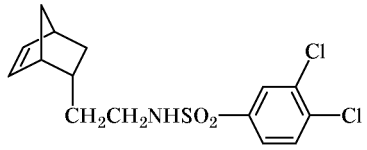
Scheme 3.



V, R = $C_6H_4NO_2$-*p* (**a**), $C_6H_4CH_3$-*p* (**b**); **VI**, R = $C_6H_4NO_2$-*p* (**a**), C_6H_5 (**b**); **VII**, R = $CH_2C_6H_5$ (**a**), $C_6H_4CH_3$-*m* (**b**).



X



XI

in **II** was derived from the different chemical shifts of 2-H and 3-H (δ 6.12 and 5.96 ppm, respectively), similar chemical shifts of protons in the bridgehead positions (1-H and 4-H; δ 2.77 and 2.76 ppm), and the position of the *endo*-6-H signal (δ 0.53 ppm) due to magnetically anisotropic effect of the exocyclic C^5-C^8 bond [2, 4, 7]. The *exo* isomer of **II** gives the following signals, δ, ppm: 6.08 (2-H), 6.04 (3-H), 2.81 (1-H), 2.51 (4-H). The ^{1}H NMR parameters of compound **II** are consistent with the criteria developed by us previously while studying stereoisomeric amines **Ia** and **Ib** and their numerous derivatives [7]. As follows from the signal intensities, the fraction of the major *endo* isomer of **II** is 86%. Comparison of of the ^{1}H NMR spectra of amines **Ib** and **II** shows some influence of the length of the side chain on the spectral parameters. The signals of **Ib** were assigned on the basis of the two-dimensional COSY spectrum. The spectra of **Va**, **VIa**, and **VIIa** are characterized by upfield shift of the C^8H_2 signals to δ 1.3–1.5 ppm and appearance of signals from C^9H_2 in the region δ 3.0–3.5 ppm. In the above series, the C^9H_2 protons of amide **VIa** are the most deshielded, as well as the other protons in its molecule. Molecules of amine **II** and its derivatives each have four methylene groups: C^6H_2, C^7H_2, C^8H_2, and C^9H_2. The corresponding proton coupling constants considerably differ from each other; e.g., for amide **VIa** they are 11.4, 8.4, 13.4, and 14.4 Hz, respectively.

Table 3 contains the ^{13}C NMR spectral parameters of compounds **Va**, **VIa**, and **VIIa**. For comparison, the data for *N*-(3,4-dichlorophenylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (**XI**) are also given (its NOESY spectrum was also measured). In the ^{13}C NMR spectra of amine **II** derivatives, recorded

Table 1. Yields, melting points, IR spectra, and elemental analyses of compounds **Va**, **Vb**, **VIa**, **VIb**, **VIIa**, **VIIb**, **VIII**, **IX**, **XIVa**, and **XIVb**

Comp. no.	Yield, %	mp,[a] °C	IR spectrum, ν, cm^{-1}	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
Va	89	85–87	3265, 3058, 1533, 1350, 1331, 1308, 1160, 720	55.93	5.39	8.74	$C_{15}H_{18}N_2O_4S$	55.90	5.59	8.70
Vb	85	77–78	3290, 1538, 1345, 1330, 1154			4.75	$C_{16}H_{21}NO_2S$	65.98	7.22	4.81
VIa	91	123–124	3293, 3057, 1640, 1556, 1522, 1347, 1279, 716	67.07	6.27	9.70	$C_{16}H_{18}N_2O_3$	67.13	6.29	9.79
VIb	71	113–114				5.91	$C_{16}H_{19}NO$	79.67	7.88	5.81
VIIa	84	86–88	3333, 3030, 1630, 1572, 1453, 1306, 1253, 720	77.43	8.07	10.30	$C_{17}H_{22}N_2O$	75.55	8.15	10.37
VIIb	87	85–86	3342, 3035, 1638, 1560, 1440, 1310, 1255, 718	75.61	8.13	10.31	$C_{17}H_{22}N_2O$	75.55	8.15	10.37
VIII	67	89–90	3360, 3200, 3070, 1550, 1326, 1250, 1180, 718	70.48	7.31	10.21	$C_{16}H_{20}N_2S$	70.59	7.35	10.29
IX	83	134–136	3070, 1750, 1700, 1581, 1344, 1240, 1180, 730			4.83	$C_{18}H_{21}NO_2$	76.32	7.42	4.95
XIVa	77	98–100	3310, 1540, 1356, 1318, 1170, 1100, 856			8.34	$C_{15}H_{18}N_2O_5S$	53.25	5.32	8.28
XIVb	89	88–90	3350, 1660, 1556, 1535, 1350, 1310, 1118, 860	63.53	5.90	9.32	$C_{16}H_{18}N_2O_4$	63.58	5.96	9.27

[a] From aqueous ethanol.

Table 2. ^{1}H NMR spectra of **Ib**, **II**, **Va**, **VIa**, **VIIa**, and **X** (δ, ppm, *J*, Hz)

Comp. no.	1-H	2-H, 3-H	4-H	5-H	*exo*-6-H	*endo*-H	*syn*-7-H, *anti*-7-H	8-H$_A$, 8-H$_B$	9-H$_A$, 9-H$_B$	NH, H$_{arom}$
Ib	2.81	6.07, 5.86, $^3J_{2,3}$ = 5.8, $^3J_{2,1}$ = 2.8, $^3J_{3,4}$ = 3.0	2.72	2.03	1.76, $^2J_{6,6}$ = 11.4, $^3J_{6,5}$ = 9.2, $^3J_{6,1}$ = 3.9	0.42, $^3J_{6,5}$ = 4.1, $^4J_{6,7s}$ = 2.6	1.37, 1.18, $^2J_{7,7}$ = 7.9	2.37, 2.29, $^2J_{8,8}$ = 12.2, $^3J_{8A,5}$ = 7.3, $^3J_{8B,5}$ = 8.2	–	1.21 (NH)
II	2.77	6.12, 5.92, $^3J_{2,3}$ = 5.4, $^3J_{2,1}$ = 2.7, $^3J_{3,4}$ = 3.0	2.76	2.04	1.85, $^2J_{6,6}$ = 11.4, $^3J_{6,5}$ = 9.3, $^3J_{6,1}$ = 3.8	0.53, $^3J_{6,5}$ = 4.0, $^4J_{6,7s}$ = 2.3	1.38, 1.22, $^2J_{7,7}$ = 8.4	1.32, 1.26, $^2J_{8,8}$ = 12.6, $^3J_{8A,5}$ = 5.4, $^3J_{8B,5}$ = 6.0	2.79, 2.66, $^2J_{9,9}$ = 14.7, $^3J_{9A,8}$ = 7.2, $^3J_{9B,8}$ = 7.2	1.56 (NH)
Va	2.81	6.17, 5.89, $^3J_{2,3}$ = 5.7, $^3J_{2,1}$ = 3.0, $^3J_{3,4}$ = 3.0	2.74	2.03	1.86, $^2J_{6,6}$ = 11.4, $^3J_{6,1}$ = 3.9	0.50, $^3J_{6,5}$ = 4.0, $^4J_{6,7s}$ = 2.7	1.44, 1.23, $^2J_{7,7}$ = 8.3	1.37, 1.30, $^2J_{8,8}$ = 12.4, $^3J_{8A,5}$ = 5.5, $^3J_{8B,5}$ = 5.6	3.27, 3.09, $^2J_{9,9}$ = 13.4, $^3J_{9A,8}$ = 7.4, $^3J_{9B,8}$ = 7.4	5.03 (NH) 8.43, 8.13
VIa	2.84	6.17, 5.96, $^3J_{2,3}$ = 5.7, $^3J_{2,1}$ = 3.0, $^3J_{3,4}$ = 2.7	2.83	2.08	1.92, $^2J_{6,6}$ = 11.4, $^3J_{6,5}$ = 9.1, $^3J_{6,1}$ = 3.8	0.59, $^3J_{6,5}$ = 4.3, $^4J_{6,7s}$ = 2.7	1.51, 1.26, $^2J_{7,7}$ = 8.4	1.46, 1.40, $^2J_{8,8}$ = 13.4, $^3J_{8A,5}$ = 7.4, $^3J_{8B,5}$ = 7.4	3.54, 3.46, $^2J_{9,9}$ = 14.4, $^3J_{9A,8}$ = 7.1, $^3J_{9B,8}$ = 6.6	6.46 (NH) 8.27, 7.96
VIIa	2.82	6.17, 5.97, $^3J_{2,3}$ = 5.7, $^3J_{2,1}$ = 3.0, $^3J_{3,4}$ = 2.7	2.79	2.01	1.88, $^2J_{6,6}$ = 11.3, $^3J_{6,5}$ = 9.0, $^3J_{6,1}$ = 3.7	0.55, $^3J_{6,5}$ = 4.0, $^4J_{6,7s}$ = 2.7	1.45, 1.26, $^2J_{7,7}$ = 7.8	1.37, 1.32	3.17, 3.14, $^3J_{9,9}$ = 13.6, $^3J_{9A,8}$ = 7.4, $^3J_{9B,8}$ = 7.0	5.38, 5.01 (NH) 7.32
X	2.75	6.08, 5.73, $^3J_{2,3}$ = 5.8, $^3J_{2,1}$ = 3.0, $^3J_{3,4}$ = 2.8	2.73	2.12	1.74, $^2J_{6,6}$ = 11.8, $^3J_{6,5}$ = 8.9, $^3J_{6,1}$ = 3.8	0.40, $^3J_{6,5}$ = 4.0, $^4J_{6,7s}$ = 2.6	1.38, 1.15, $^2J_{7,7}$ = 8.4	2.67, 2.58, $^2J_{8,8}$ = 12.6	–	4.79 (NH) 8.31, 7.98

by the Rubenstein–Nakashima technique, the C^7, C^8, and C^9 signals are located at δ_C 49.6–49.7, 39.8–42.5, and 34.6–35.2 ppm, respectively. All compounds have nonequivalent carbon atoms at the double bond, δ_C 137.3–137.8 and 131.8–132.3 ppm.

Urea **VIIa** shows in the ^{1}H NMR spectrum signals from the benzyl group at δ 4.55 and 7.32 ppm and two nonequivalent NH protons at δ 5.38 and 5.01 ppm. Analogous NH protons in compounds **Va** and **VIa** give rise to signals at δ 5.03 and 6.46 ppm. The carbonyl carbon signals of **VIa** and **VIIa** appear in the ^{13}C NMR spectra at δ_C 165.5 and 158.7 ppm, respectively, and methylene carbon nucleus of the benzyl group gives a signal at δ_C 44.4 ppm.

We also continued our studies on heterocyclization by the action of peroxy acids [16] of compounds in which arenesulfonamide and arenecarboxamide fragments are separated from the norbornene framework by different numbers of methylene units. According to our previous data, reactions of substituted *endo*-5-aminomethylbicyclo[2.2.1]hept-2-enes with peroxyphthalic acid take different pathways, depending on the substituent on the nitrogen. In particular, carboxamide derivatives are converted into epoxy compounds **XII** [17], whereas sulfonamides give rise to substituted 4-azatricyclo[4.2.1.0^{3,7}]nonanes (azabrendanes) **XIII** [18] (Scheme 4).

Scheme 4.

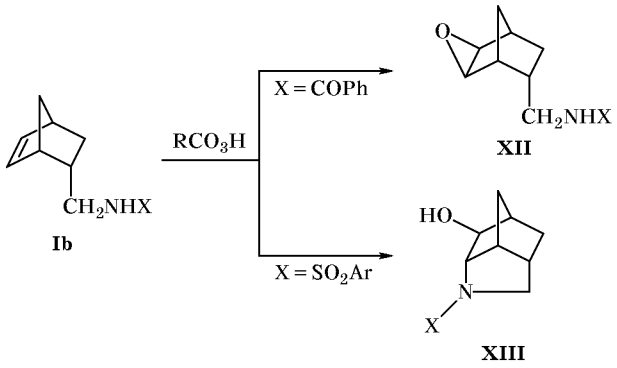
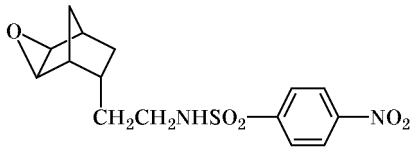


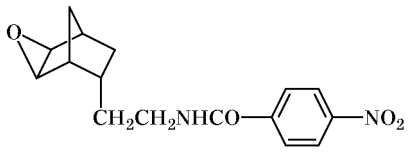
Table 3. ^{13}C NMR spectra of 5-(2-aminoethyl)bicyclo[2.2.1]hept-2-ene derivatives, δ_C, ppm

Comp. no.	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C=O, C_{arom}
Va	42.71	137.78	131.84	45.31	35.84	32.08	49.66	34.75	42.53	146.08, 136.59, 128.42, 124.56
VIa	42.61	137.64	132.07	45.58	36.46	32.36	49.72	34.62	39.84	165.52, 130.76, 128.18, 123.86, 123.59
VIIa	42.56	137.32	132.27	45.50	36.23	32.28	49.66	35.24	39.79	158.70, 139.58, 128.64, 127.41 127.22, 44.42
XI	42.3	138.2	131.5	43.9	38.9	30.0	49.5	47.2	–	139.8, 137.4, 133.7, 131.1, 126.1

The possibility for heterocyclization with formation of six- and seven-membered analogs of azabrendanes **XIII** was studied using compounds **Va** and **VIa** as examples. The reactions were carried out in chloroform with peroxyphthalic acid generated *in situ* from phthalic anhydride and 40–45% aqueous hydrogen peroxide [18]. As a result, we isolated epoxy derivatives **XIVa** and **XIVb** as the only reaction products (Table 1). Their structure was confirmed by the IR and ^1H NMR spectra.



XIVa



XIVb

The IR spectra of **XIVa** and **XIVb** contain a band at 860–850 cm^{-1}, which is typical of stretching vibrations of the oxirane C–O bond in epoxynorbornanes [16]. Also, absorption bands due to NH group (3350–3310 cm^{-1}) and *p*-nitrophenylsulfonyl or *p*-nitrobenzoyl substituent were present (Table 1).

The ^1H NMR parameters of compounds **XIVa** and **XIVb** are given in Table 4. In the region δ 3.05–3.25 ppm we observed two doublets from protons of the oxirane ring and a characteristic upfield signal at δ 0.75 (0.80) ppm, belonging to one of the bridge protons (*anti*-7-H). It is located above the oxirane ring plane and is strongly shielded by the latter.

Our results show that, unlike sulfonamides derived from aminomethylnorbornene **Ib**, no heterocyclization of their analogs having two methylene units between the amino group and bicyclic fragment occurs in reactions with peroxy acids.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films or KBr pellets. The ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-300 instrument at 300 and 75.4 MHz, respectively, using chloroform-*d* as solvent and HMDS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent and iodine vapor as developer.

Bicyclo[2.2.1]hept-2-ene-5-carbaldehyde (III). Freshly distilled cyclopentadiene [19], 17.2 g (21.5 ml, 0.26 mol) was slowly added with stirring to 14.6 g (17.3 ml, 0.26 mol) of acrolein. When the reaction was over (TLC), the mixture was subjected to vacuum distillation. Yield of **III** 26 g (82%), bp 62–64°C (16 mm), n_D^{20} = 1.4876; published data [19]: bp 52.4°C (6 mm), n_D^{20} = 1.4883.

5-Nitroethenylbicyclo[2.2.1]hept-2-ene (IV). A solution of 6.2 g (0.154 mol) of sodium hydroxide in 20 ml of an ice–water mixture was added to a mixture of 15 g (0.123 mol) of aldehyde **III**, 7.4 g (6.5 ml, 0.123 mol) of nitromethane, and 50 ml of methanol at such a rate that the temperature did not exceed 10–15°C (on cooling with ice–NaCl). The mixture was kept for 15–20 min, and 60–80 ml of cold water containing crushed ice was added. The resulting transparent solution was poured with stirring into excess 20% hydrochloric acid, and the organic phase (containing mainly nitro derivative **IV**) was

Table 4. ^{1}H NMR spectra of epoxynorbornanes **XIVa** and **XIVb** (δ, ppm, *J*, Hz)

Comp. no.	1-H	2-H, 3-H	4-H	5-H	*exo*-6-H	*endo*-H	*syn*-7-H, *anti*-7-H	8-H$_A$, 8-H$_B$	9-H$_A$, 9-H$_B$	NH, H$_{arom}$
XIVa	2.47	3.12, 3.06	2.35	1.92	1.75, $^2J_{6,6}$ = 13.2, $^3J_{6,5}$ = 9.2, $^3J_{6,1}$ = 4.2	0.87	1.33, 0.75, $^2J_{7,7}$ = 9.6	1.67, 1.54, $^2J_{8,8}$ = 13.8, $^3J_{8A,5}$ = 7.5, $^3J_{8B,5}$ = 8.4	3.02, 2.99, $^2J_{9,9}$ = 13.5	4.94 (NH) 8.36, 8.07
XIVb	2.51	3.24, 3.16, $^3J_{2,3}$ = 3.3	2.47	1.98	1.84, $^2J_{6,6}$ = 11.7, $^3J_{6,5}$ = 9.4, $^3J_{6,1}$ = 4.2	0.85, $^3J_{6,5}$ = 4.0, $^4J_{6,7s}$ = 2.0	1.36, 0.80, $^2J_{7,7}$ = 9.6	1.78, 1.66, $^2J_{8,8}$ = 13.8, $^3J_{8A,5}$ = 6.6, $^3J_{8B,5}$ = 7.5	3.50, 3.47, $^2J_{9,9}$ = 13.5	6.38 (NH) 8.29, 7.93

separated, dried, and distilled in vacuo. Yield 73%, bp 107–108°C (5 mm), n_D^{20} = 1.5294; published data [12]: bp 102–104°C (0.6 mm), n_D^{20} = 1.5338.

5-(2-Aminoethyl)bicyclo[2.2.1]hept-2-ene (II). A solution of 12 g (0.073 mol) of nitro derivative **IV** in 20 ml of dry diethyl ether was added dropwise with stirring to a suspension of 14 g (0.365 mol) of lithium aluminum hydride in 100 ml of dry diethyl ether at such a rate that the mixture moderately boiled. The mixture was then stirred at 40°C until the reaction was complete (TLC). Excess $LiAlH_4$ was slowly decomposed by adding moist diethyl ether and water, the precipitate was filtered off, the organic phase was separated and dried over calcined magnesium sulfate, the solvent was distilled off, and the residue was distilled under reduced pressure. Yield of amine **II** 74%, bp 93–94°C (30 mm), n_D^{20} = 1.4976; published data [12]: bp 48°C (0.6 mm), n_D^{20} = 1.4985.

5-[2-(*p*-Nitrophenylsulfonylamino)ethyl]bicyclo-[2.2.1]hept-2-ene (Va). A solution of 0.58 g (0.0026 mmol) of *p*-nitrobenzenesulfonyl chloride in 10 ml of diethyl ether was added dropwise with stirring to a mixture of 0.35 g (0.0026 mol) of amine **II** and 0.51 g (0.42 ml, 0.0026 mol) of 20% aqueous sodium hydroxide in 15 ml of diethyl ether. The mixture was stirred until the reaction was complete (TLC), the solvent was removed, the residue was dissolved in 20 ml of chloroform–water (1:1), the organic phase was separated, dried, and evaporated, and the residue was recrystallized from aqueous ethanol.

5-[2-(*p*-Tolylsulfonylamino)ethyl]bicyclo[2.2.1]-hept-2-ene (Vb) was synthesized in a similar way from 0.15 g (0.0011 mol) of amine **II** and 0.21 g (0.0011 mol) of *p*-toluenesulfonyl chloride (Table 1).

5-[2-(*p*-Nitrobenzoylamino)ethyl]bicyclo[2.2.1]-hept-2-ene (VIa). A solution of 0.52 g (0.0028 mol) of *p*-nitrobenzoyl chloride in 10 ml of dry chloroform was added dropwise with stirring to a mixture of 0.35 g (0.0026 mol) of amine **II** and 0.41 g (0.42 ml, 0.0052 mol) of pyridine in 20 ml of dry chloroform. The mixture was stirred at room temperature until the reaction was complete (TLC) and was then washed with three portions of water, 20% hydrochloric acid, and water again. The organic layer was separated and dried over calcined magnesium sulfate, the solvent was removed, and the product was recrystallized from aqueous ethanol.

5-(2-Benzoylaminoethyl)bicyclo[2.2.1]hept-2-ene (VIb) was synthesized in a similar way from 0.12 g (0.9 mmol) of amine **II** and 0.12 g (0.9 mmol) of benzoyl chloride.

5-[2-(*N'*-Benzylureido)ethyl]bicyclo[2.2.1]hept-2-ene (VIIa). Benzyl isocyanate, 0.15 g (0.0011 mol), was added to a solution of 0.15 g (0.0011 mol) of amine **II** in 2 ml of benzene. When the reaction was complete, the crystals were filtered off, washed with benzene, dried, and recrystallized from aqueous ethanol (Tables 1–3). The same procedure was used to synthesize compounds **VIIb** and **VIII**.

***N*-[2-(Bicyclo[2.2.1]hept-5-en-2-yl)ethyl]endic imide (IX).** Amine **II**, 0.1 g (0.73 mmol), was added to a solution of 0.12 g (0.73 mmol) of endic anhydride in 2 ml of benzene. The precipitate was filtered off, washed with benzene, and recrystallized from aqueous ethanol.

***exo*-2,3-Epoxy-5-[2-(*p*-nitrophenylsulfonyl-amino)ethyl]bicyclo[2.2.1]heptane (XIVa).** A mixture of 0.15 g (0.47 mmol) of sulfonamide **Va**, 0.03 g (0.47 mmol) of urea, 0.08 ml (0.94 mmol) of 35% hydrogen peroxide, and 0.14 g (0.94 mmol) of powdered phthalic anhydride in 20 ml of chloroform was stirred until the reaction was complete (TLC). The mixture was neutralized with a saturated solution of sodium

hydrogen carbonate, the organic layer was separated and dried over calcined magnesium sulfate, the solvent was removed, and the residue was purified by chromatography on silica gel using diethyl ether as eluent.

***exo*-2,3-Epoxy-5-[2-(*p*-nitrobenzoylamino)ethyl]-bicyclo[2.2.1]heptane (XIVb)** was synthesized in a similar way (Tables 1, 4).

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