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Synthesis and Reactivity of Amines Containing Several Cage-like Fragments

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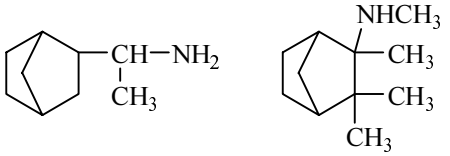
Abstract—By reaction of bicyclo[2.2.1]hept-5-en-*exo*- and *endo*-2-ylmethylamine, *exo*-5,6-epoxybicyclo[2.2.1]hept-*exo*-2-ylmethylamine and benzylamine with 1-adamantanecarbonyl chloride, 1,3-adamantanedicarbonyl dichloride, and 1,3-adamantanediacetyl dichloride amides were obtained with one, two, and three cage-like fragments that were reduced to amines by lithium aluminum hydride. The reactivity of the amines was evaluated with the use of semiempirical quantum-chemical method PM3. Derivatives of the amines were prepared by reactions with arenesulfonyl chlorides, *p*-nitrobenzoyl chloride, succinic and endic anhydrides, *p*-toluenesulfonyl and *m*-tolyl isocyanates, phenyl isothiocyanate, and *p*-nitrophenyloxirane. The structure of the new compounds was supported by analysis of their IR and ^{1}H NMR spectra. The dependence of some reaction conditions was observed on the number and remoteness of the cage-like fragments from the reaction centers of the amines.

Amines from the norbornene and norbornane series exhibit versatile pharmacological activity. Antiviral agents were found among them [1], for example, amine **Ia** introduced into the medical practice as hydrochloride (deutiforin) [2]. Mecamilamine **Ib** is known as ganglioblocking preparation [3]. Amines exhibit styptic and topical anesthetic action, they are indicators of psychic and physical dystrophy, remove fatigue [3].

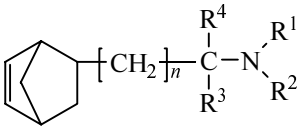
Amines of the **Ic** group are strong analgetics; depending on the number *n* and character of the substituents attached to carbon and nitrogen atoms these compounds either increase or decrease the blood pressure and show bactericidal properties [4]. Derivatives of bicyclo[2.2.1]-hept-5-en-2-ylmethylamine containing piperidine, pyrrolidine and other moieties resemble by their activity the amines of the **Ic** group: specific inhibitors have been found among them for the pathogenic flora, tubercle bacillus, and other bacteria [5]. Up till now a single amine with two cage-like fragments was described whose derivatives (**Id**, R = $COCH_3$, CONHAr) possessed anti-arrhythmic, hypoglycemic, and hypotensive activity [6].

Taking into account the favorable effect of the bicyclic carbon cage-like structure on the pharmacological characteristics of amines we aimed this research to development of synthetic procedures and to study of reactivity of amines with norbornene and adamantane skeleton, of the dependence of their chemical behavior on the number and relative position of the cage-like fragments. The amines were prepared by reduction with lithium aluminum hydride of adamantanecarboxamides; a similar procedure had been previously used in the synthesis of alkyl-(aralkyl)norbornenylmethylamines [7]. In amides preparation 1-adamantanecarbonyl chloride (**IIa**), 1,3-adamantanedicarbonyl dichloride (**IIb**), and 1,3-adamantanediacetyl dichloride (**IIc**) were used.

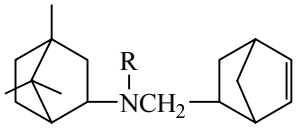


Ia

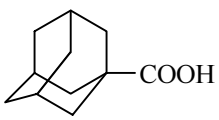
Ib



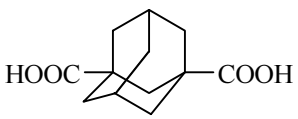
Ic



Id



IIa



IIb

IIc

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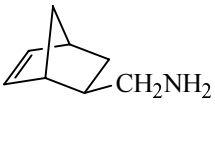
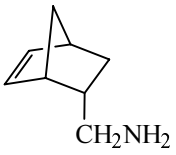
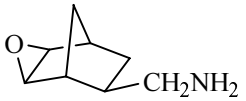
As amine components bicyclo[2.2.1]hept-5-en-*exo*- and *endo*-2-ylmethylamines (**IIIa** and **IIIb**), and epoxy derivative **IIIc** of amine **IIIa** were chosen. Benzylamine (**IIId**) was also used for comparison. Synthesis of amines **IIIa** and **IIIb** was carried out by known procedures [8] reducing the sterically uniform bicyclo[2.2.1]hept-2-en-*exo*- and *endo*-5-ylcarbonitriles, products obtained by diene synthesis from cyclopentadiene and acrylonitrile. Epoxyamine **IIIc** was preperad by the method we had developed earlier [9].



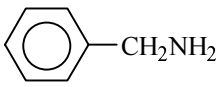
IIIa



IIIb



IIIc



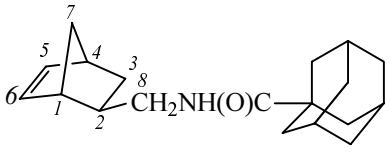
IIId

Crystalline amides **IVa–IVf** were obtained by reactions of acyl chlorides **IIa–IIc** with amines **IIIa–IIId** in the presence of triethylamine by procedure [7]. The preparation of amide **IVb** was formerly described in [10].

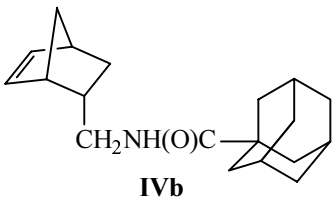
The IR spectra of amides contain absorption bands of the secondary amide groups in the regions 1635–1622, 1544–1526, and 1270–1243 cm^{-1} corresponding to the stretching vibrations of the carbonyl groups "amide I", to the bending vibrations of the NH bond "amide II", and to the stretching vibrations of the C–N bond "amide III", and also an absorption band in the region 3400–3330 cm^{-1} (ν_{NH}) [11].

In the IR spectra of amides with a norbornene fragment appears a characteristic absorption in the region 3060–3030 ($\nu_{=C-H}$) and 725–700 cm^{-1} ($\delta_{=C-H}$) [12]. The position of the latter band is governed by the stereochemical features of amides: in the IR spectrum of *exo*-isomer **IVa** this band is close to the lower (712 cm^{-1}), and that of the *endo*-stereoisomers to the higher limit of the range. This band lacks in the IR spectrum of epoxyamide **IVc** but a band is observed in the region 851 cm^{-1} characteristic of vibrations of the C–O bonds in the three-membered ring of epoxynorbornanes [13].

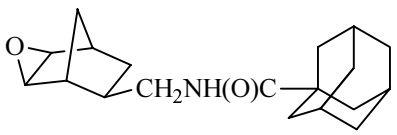
Parameters of the ^{1}H NMR spectra of amides **IVa–IVd** are presented in Table 1. The *exo*- and *endo*-orientation of substituents in the norbornene skeleton was confirmed by criteria previously developed for stereoisomeric amines **IIIa** and **IIIb** and for the corresponding amides containing aromatic moieties [7]. In keeping with the known criteria in the spectra of *endo*-isomers **IVb, IVd**, and **IVe** a significant nonequivalence (up to 0.2 ppm) is observed in the protons of the olefin fragment (H^5, H^6) and protons attached to atom C^3 (H^{3x} and H^{3n}) (up to 1.3 ppm). Also a slight nonequivalence characterizes the bridgehead protons (H^1 and H^4) (< 0.1 ppm). On the contrary, in the spectra of *exo*-stereoisomers **IVa** and **IVc** the protons at the double bond and in the epoxy ring



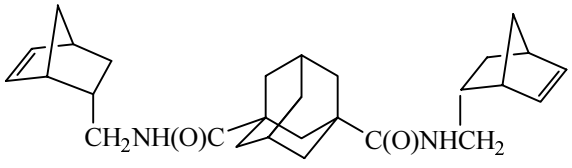
IVa



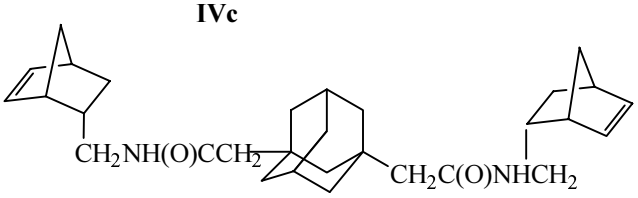
IVb



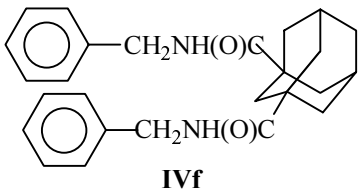
IVc



IVd



IVe



IVf

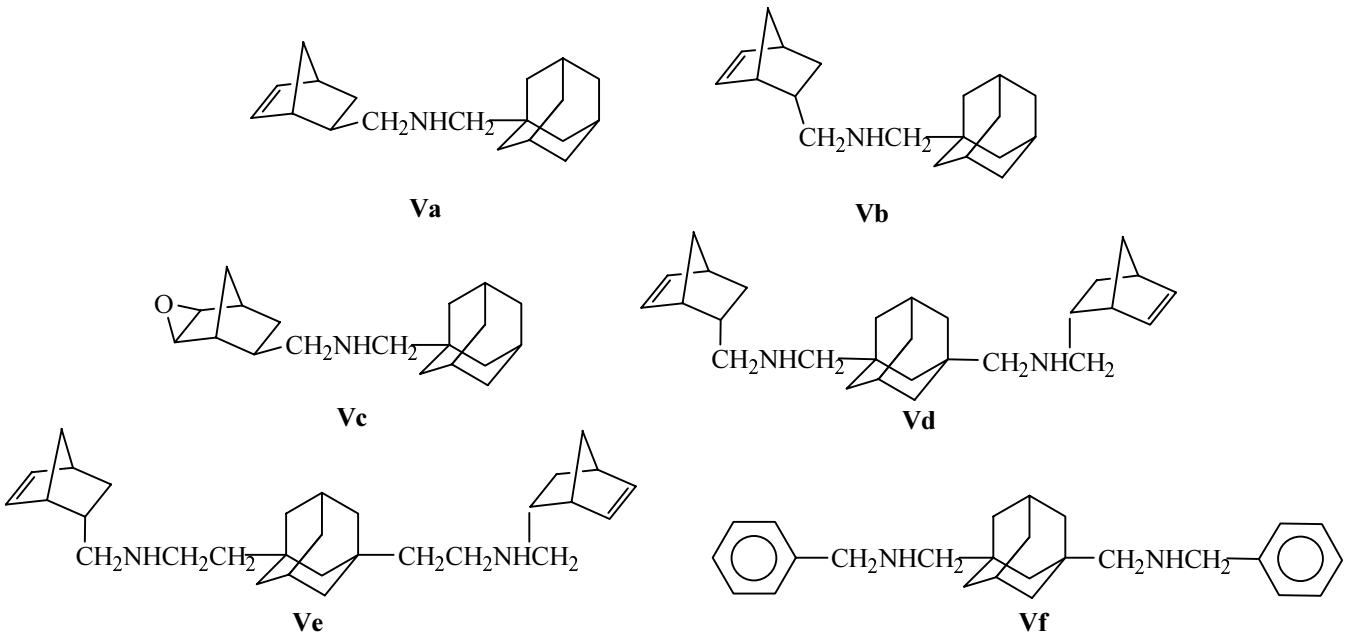
Table 1. Parameters of ^{1}H NMR spectra of amides **IVa–IVe** and amines **Va**, **Vb**, **Vd**, and **Ve**, δ, ppm (*J*, Hz)

Compd. no.	H^1	H^2	H^{3X}	H^{3n}	H^4	H^5, H^6	H^{7s}, H^{7a}	H^{8A}, H^{8B}	Substituent
IVa	2.58	1.43	1.53 ($^2J_{3x,3n}$ 11.2, $^3J_{3X,2}$ 7.6, $^3J_{3X,4}$ 3.6)	1.16 ($^3J_{3n,2}$ 4.0, $^3J_{3n,7s}$ 2.6)	2.83	6.07	1.25, 1.34 ($^2J_{7s,7a}$ 8.4)	3.25, 3.29	1.50–1.95 (15H, Ad), 5.56 (1H, NH)
IVb	2.78	2.30	1.86 ($^2J_{3x,3n}$ 12.4)	0.52	2.74	6.11, 6.06	1.35, 1.22 ($^2J_{7s,7a}$ 8.1)	2.93, 2.86 ($^2J_{8A,8B}$ 14.3, $^3J_{8A,5}$ 7.1, $^3J_{8B,5}$ 6.6)	1.55–1.90 (15H, Ad), 6.08 (1H, NH)
IVc	2.29	1.30	1.47 ($^2J_{3x,3n}$ 12.4, $^3J_{3X,2}$ 8.4, $^3J_{3X,4}$ 4.0)	1.12 ($^3J_{3n,2}$ 4.4, $^3J_{3n,7s}$ 4.0)	2.4	3.10, 3.07 ($^3J_{5,6}$ 4.0)	1.21, 0.88 ($^2J_{7s,7a}$ 10.4)	3.15, 3.13	1.50–1.90 (15H, Ad), 5.66 (1H, NH)
IVd	2.78	2.41	1.38 ($^2J_{3x,3n}$ 11.8)	0.51	2.68	6.00, 5.87	1.26, 1.12 ($^2J_{7s,7a}$ 8.6)	2.80, 3.00	1.50–2.00 (15H, Ad), 8.17 (2H, NH)
IVe	2.90	2.24	1.84 ($^2J_{3x,3n}$ 11.4, $^3J_{3X,2}$ 9.1, $^3J_{3X,4}$ 3.9)	0.56 ($^3J_{3n,2}$ 3.9, $^3J_{3n,7s}$ 2.1)	2.81	6.17, 5.96 ($^3J_{5,6}$ 5.4, $^3J_{5,4}$ 2.4, $^3J_{6,1}$ 2.7)	1.26, 1.22 ($^2J_{7s,7a}$ 7.6)	2.97, 2.94	1.50–2.00 (15H, Ad), 5.56 (2H, NH), 4.01, 4.11 (4H, 2CH_2 Ad)
Va	2.62	1.44	1.20 ($^2J_{3x,3n}$ 11.6)	1.10 ($^3J_{3n,2}$ 3.8, $^3J_{3n,7s}$ 2.6)	2.79	6.09, 6.04 ($^3J_{5,6}$ 6.4, $^3J_{5,4}$ 2.8, $^3J_{6,1}$ 3.0)	1.24, 1.30 ($^2J_{7s,7a}$ 8.4)	2.27, 2.20	1.50–2.00 (15H, Ad), 2.57–2.68 (2H, CH_2Ad), 2.79 (1H, NH)
Vb	2.76	2.30	1.76 ($^2J_{3x,3n}$ 11.4)	0.48 ($^3J_{3n,7s}$ 2.5)	2.82	6.12, 5.88 ($^3J_{5,6}$ 6.1, $^3J_{5,4}$ 2.6, $^3J_{6,1}$ 2.6)	1.41, 1.22 ($^2J_{7s,7a}$ 8.8)	2.30, 2.20	1.50–2.00 (15H, Ad), 3.17 (2H, CH_2Ad), 3.18 (1H, NH)
Vd	2.65	2.66	1.70 ($^2J_{3x,3n}$ 11.0)	0.39	2.73	6.03, 5.78	1.25, 1.30 ($^2J_{7s,7a}$ 8.4)	2.15, 2.23	1.50–2.00 (14H, Ad), 2.20–2.25 (4H, 2CH_2Ad), 3.15 (2H, 2NH)
Ve	2.81	2.25	1.84 ($^2J_{3x,3n}$ 11.4)	0.56 ($^3J_{3n,2}$ 3.6, $^3J_{3n,7s}$ 2.4)	2.89	6.16, 5.96 ($^3J_{5,6}$ 5.7, $^3J_{5,4}$ 2.4, $^3J_{6,1}$ 2.6)	1.27, 1.19 ($^2J_{7s,7a}$ 8.1)	2.28, 2.22	1.35–2.00 (14H, Ad), 2.80 (2H, 2NH), 2.96–2.92 (4H, 2CH_2Ad), 3.69, 3.48 (4H, 2CH_2NH)

(H^5 and H^6) and also the protons H^{3x} H^{3n} are nearly equivalent, but a significant difference is observed in the positions of protons H^1 and H^4. For the spectra of amides containing additionally adamantane fragments **IVa–IVd** and **IVf** the most convincing criterium is related to the resonance of protons at C^3 atom that is governed by the contribution of the magnetic anisotropy of the exocyclic C^2–C^8 bond. The proton signals from the NH groups are located in the region 5.5–8.2 ppm. In the spectrum of amide **IVf** the signals at 4.43 (4 H), 5.85 (2 H), and 7.25 ppm (10 H) confirm the presence of two benzylamine groups in the amide molecule.

The reduction of amides **IVa–IVf** with lithium aluminum hydride in a boiling anhydrous ether (TLC monitoring) afforded oily amines containing several carbon cage-like structures **Va–Vf** that were additionally characterized by preparation of the corresponding crystalline hydrochlorides **VIb–VIf**.

The IR spectra of amines lack bands "amide I" but possess absorption bands in the region 3400–3350 cm^{-1} (ν_{NH}) [11]. In the spectra of compounds containing norbornene moieties appear absorption bands in the region 3065–3030 and 730–710 cm^{-1} ($\nu_{=C-H}$, $\delta_{=C-H}$). The R_f values (ether) of amines are fairly high (0.83–0.96), for



diamines **Vd–Vf** they equal to 0.20–0.30. In the IR spectra of amines hydrochlorides **VIb–VIf** the absorption bands are observed in the region 2725–2700 cm^{-1} ($\nu_{as}{}^{+}NH_2$) and also bands corresponding to the unsaturated parts of the salt molecules [12].

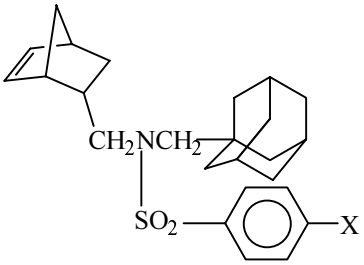
The parameters of ^1H NMR spectra of amines are compiled in Table 1. They differ from the spectra of initial amides by an upfield shift of proton signals from H^{8A} and H^{8B} and by appearance of proton signals from the methylene group CH_2Ad located in the region 2.60–3.20 ppm; in the same region are also situated the proton signals from both amino groups. In the spectrum of amine **Vd**, like in the spectra of the other substituted norbornenes, signals are present from the protons H^5 and H^6 (doublets of doublets in the region 6.02 and 5.79 ppm), and also a resonance of proton H^{3n} taking a special place in the spectra of this and other *endo*-stereoisomers (0.39 ppm). In the spectrum of amine **Vf** the protons of benzyl groups give rise to signals in the region 3.71 and 7.25 ppm.

In the molecules of amines **Va–Vf** one or several amino groups are surrounded by cage-like fragments located at various distance. The electron density distribution in the molecules of the amines we studied by quantum-chemical calculations carried out by semiempirical method PM3 [14]. The proton affinity found as the difference between the heat of formation of the protonated and free amines **Va–Vc** was estimated at 857.61, 861.97, and 846.93 kJ mol^{-1} respectively. These values are greater that the proton affinity of the initial primary amines **IIIa–IIIc** and of the 1-adamantylmethylamine (840.08, 845.03, 828.45, and 847.28 kJ mol^{-1} respectively). In the molecules of the secondary amines the HOMO is localized on the nitrogen atoms, and OMO II on the carbons of the ethylene fragments of the norbornene carbon skeleton. The thorough study of reactivity was carried out by an example of amine **Vb** which was converted into sulfonamides (**VIIa–VIIc** , X = NO_2, Cl, CH_3), carboxamide **VIId**, amido acids **VIIe** and **VIIf**, ureas **VIIg** and **VIIh**, and thiourea **VIIi**.

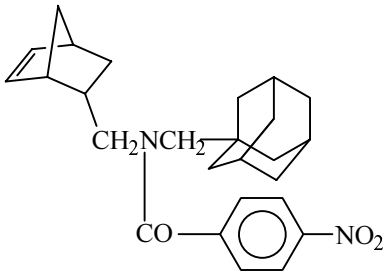
The amine was brought into a reaction with an available epoxide, *p*-nitrophenyloxirane, an intermediate compound in manufacturing the antibiotic chloramphenicol [15].

Compounds **VIIa, VIIb, VIId–VIIg** were obtained in a crystalline state, and the other compounds were oily substances purified by chromatography on columns packed with silica gel.

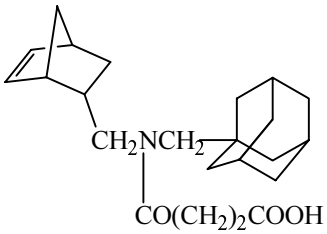
Sulfonamides **VIIa–VIIc** were prepared by two procedures: in a two-phase system (ether–water) at equimolar ratio of the reagents (amine, sulfonyl chloride, and sodium hydroxide) and in a one-phase system (in chloroform with pyridine as base). Although the arylsulfonylation of the initial primary amines **IIIa–IIId** had been previously performed along both pathways at room temperature [16], we succeeded in carrying out the reactions with amine **Vb** only in the one-phase mode at 60°C. The heating was also required in preparation of amide **VIId** by the reaction of amine with *p*-nitrobenzoyl chloride in chloroform in the presence of a base; the reactions with succinic and endic anhydrides were



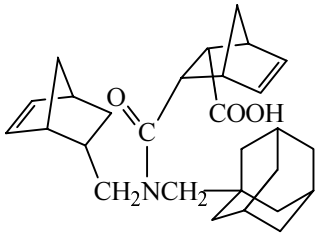
VIIa–c



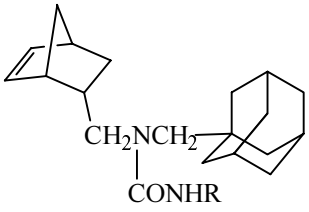
VIId



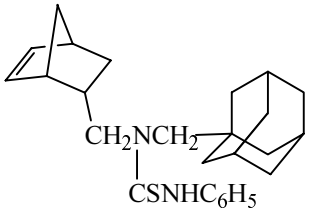
VIIe



VIIf

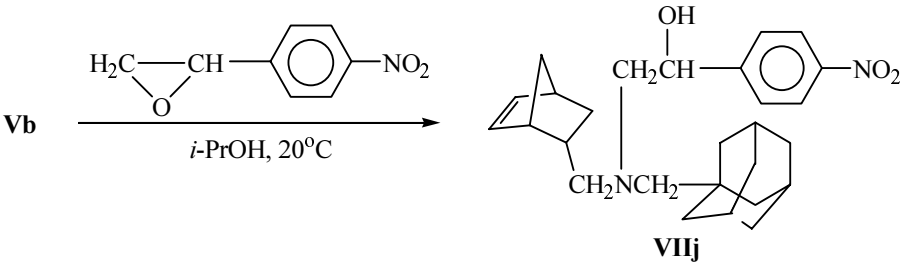


VIIg, h



VIIi

VII, X = NO_2 (**a**), Cl (**b**), CH_3 (**c**); R = $SO_2C_6H_4CH_3$-*p* (**g**), $C_6H_4CH_3$-*m* (**h**).



VIIj

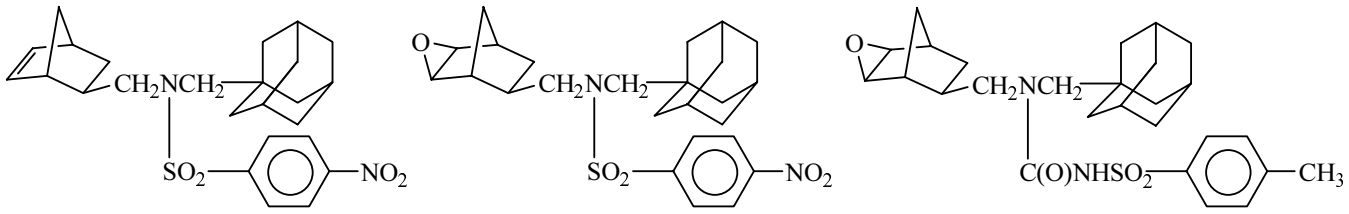
performed by short heating in ethyl acetate and benzene respectively. The other processes (with *p*-toluenesulfonyl and *m*-tolyl isocyanates, and with phenyl isothiocyanate) were performed in benzene at room temperature.

In the IR spectra of sulfonamides **VIIa–VIIc** and of sulfonylurea **VIIg** absorption bands are observed originating from bond vibrations in the sulfonyl group (1352–1340 and 1190–1180 cm^{-1}). In the spectra of compounds **VIId–VIIh** absorption bands of the amide moiety are present: "amide I" in the region 1650–1605 cm^{-1} ($\nu_{C=O}$) and "amide III" in the region 1280–1270 cm^{-1} (ν_{C-N}), but the absorption from the N–H bonds is lacking in the spectra except for those of ureas **VIIg** and **VIIh** [11]. In the IR spectrum of the thiourea lacks the absorption band of the carbonyl group, and a band is observed in the region 1310 cm^{-1} ($\nu_{C=S}$). The spectra of amido acids **VIIe** and **VIIf** contain the bands in the region 1712 and 1710 cm^{-1} belonging to the carbonyls in the carboxy groups [11]. In the spectrum of aminoalcohol **VIIj** the observed absorption bands correspond to hydroxy (3395 cm^{-1}) and nitro (1534 and 1350 cm^{-1}) groups. The absorption band of the strained double bond in the most spectra is overlapped by the bands originating from vibrations of the bonds in the aromatic fragments.

Under similar conditions the related amines **Va** and **Vb** reacted with *p*-nitrophenylsulfonyl chloride and *p*-toluenesulfonyl isocyanate affording compounds **VIIIa–VIIIc**.

The chemoselective transformation of epoxyamine **Vc** occurring with the retention of the epoxy ring is due to the spatial hindrances for the attack from the rear (*endo*) side of the carbon skeleton in the absence of acid catalysts [17].

The reactions of compound **Vd** possessing two amino groups and three cage-like fragments with five versatile electrophilic reagents (*p*-nitrobenzenesulfonyl and *p*-nitrobenzoyl chlorides, succinic anhydride, *p*-toluenesulfonyl and *m*-tolyl isocyanates) afforded compounds **IXa–IXe**.



VIIIa **VIIIb** **VIIIc**

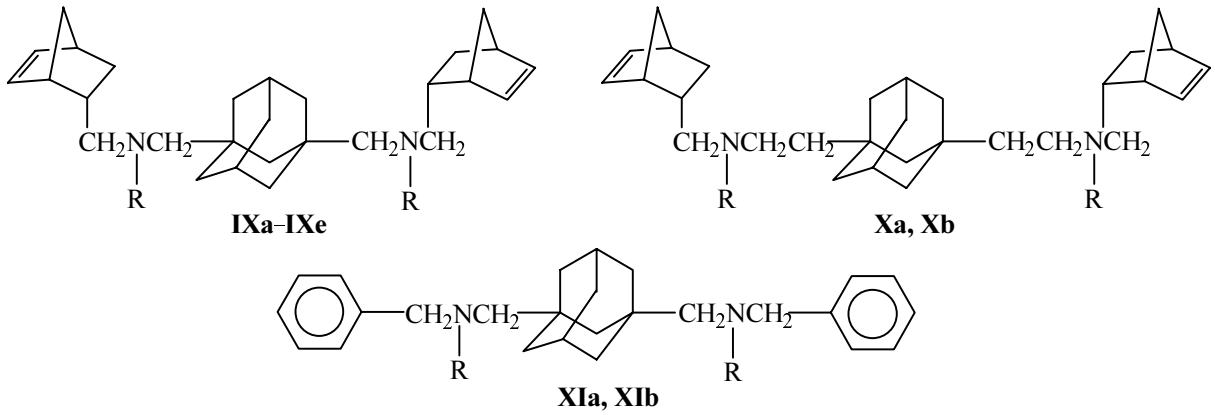
In reactions of diamine **Vd** a necessity was again observed previously found for amines **Va–Vb** to carry out arenesulfonylation and benzoylation under rigorous conditions confirming the importance of the steric factor in reactions where in the immediate vicinity of the reaction site (removed by a single methylene group) were located the cage-like fragments of norbornene, norbornane, and adamantane.

To confirm the contribution of the contiguous carbon cage-like structures we studied reactions of amine **Ve** where the cage-like fragments are further from the nitrogen (by two methylene groups), and also reactions of amine **Vf**, analog of compound **Vd** with benzyl groups instead of norbornenyl ones. The products of amines **Ve** and **Vf** were obtained in reactions with *p*-nitrobenzenesulfonyl chloride and *p*-toluenesulfonyl isocyanate (compounds **Xa, Xb** and **XIa, XIb** respectively).

In contrast to the compounds obtained before sulfonamides **Xa** and **XIa** were prepared under mild conditions (20°C) in chloroform at the common reagents ratio with the use of the same base.

Among the derivatives of amines **Va, Vc–Ve** alongside crystalline compounds a number of oily substances was obtained, in particular, amides of adamantanedicarboxylic acids **IIIb** and **IIIc**. The IR spectra of the amines derivatives contain the absorption bands corresponding to the fragments present in the molecule: sulfonamide, carboxamide, nitro groups. The parameters of ^{1}H NMR spectra of sulfonamides **VIIa, VIIb, VIIIa, VIIIb**, and **Xa** and sulfonylureas **VIIg** and **IXd** are presented in Table 2. The spectra of stereoisomers **VIIa** and **VIIIa** have considerably different positions of the signals from protons H^{2} (1.48 and 2.55 ppm), H^{3X} (1.14 and 1.62 ppm), H^{3n} (0.92 and 0.47 ppm); this difference is informative and is well consistent with the differences discussed above concerning the structure of carboxamides and the initial amines with two cage-like fragments. In the spectrum of the epoxy compound **VIIIb** the characteristic signals from the protons of the epoxy ring H^{5} and H^{6} were observed (3.31 and 3.29 ppm), and a doublet of the proton H^{7a} shifted upfield by 0.86 ppm due to the effect of the magnetic anisotropy of the three-membered ring [18]. The proton signals from the adamantane skeleton appeared in the region 1.55–2.05 ppm, and those from $C\underline{H}_2$Ad in the region 2.90–3.17 ppm

The comparison of ^{1}H NMR spectra of sulfonylureas **VIIg** and **IXd**, derivatives of *endo*-amine **IIIb**, and of adamantanecarboxylic acids **IIa** and **IIb** revealed the different ratio of signals belonging to nuclei of norbornene and adamantine skeletons.



IXa–IXe **Xa, Xb**

XIa, XIb

R = $SO_2C_6H_4NO_2$-*p* (**IXa–XIa**), $C(O)C_6H_4NO_2$-*p* (**IXb**), $C(O)CH_2CH_2COOH$ (**IXc**), $C(O)NHSO_2C_6H_4CH_3$-*p* (**IXd, Xb, XIb**), $C(O)NHC_6H_4CH_3$-*m* (**IXe**).

Table 2. ^{1}H NMR spectra of derivatives **VIIa–VIIg**, **VIIIa**, **VIIIb, IXd, Xa** obtained from amines **Va–Ve**, δ, ppm (*J*, Hz)

Compd. no.	H^1	H^2	H^{3X}	H^{3n}	H^4	H^5, H^6	H^{7s}, H^{7a}	H^{8A}, H^{8B}	Substituent
VIIa	2.85	2.55	1.62	0.47	2.65	6.08, 5.90	1.28, 1.22	2.80–2.90	1.50–2.00 (15H, Ad), 2.90–3.10 (2H, CH_2Ad), 8.03, 8.25 (4H, H_{arom})
VIIb	2.70	2.26	1.52 ($^2J_{3x,3n}$ 12.5)	0.40 ($^3J_{3n,2}$ 2.5, $^3J_{3n,7s}$ 2.4)	2.65	6.12, 5.78 ($^3J_{5,6}$ 6.2)	1.37, 1.28 ($^2J_{7s,7a}$ 8.6)	2.80–2.90	1.50–2.00 (15H, Ad), 3.00–3.10 (2H, CH_2Ad), 7.85, 7.75 (4H, H_{arom})
VIIc	2.92	2.35	1.50–1.80	0.58	2.80	6.20, 5.95	1.28, 1.22	2.85–3.00	1.50–2.00 (15H, Ad), 3.10–3.20 (2H, CH_2Ad), 7.15, 7.65 (4H, H_{arom})
VIIe	2.89	2.30–2.40	1.85 ($^2J_{3x,3n}$ 11.4, $^3J_{3x,2}$ 8.4, $^3J_{3x,4}$ 3.9)	0.54 ($^3J_{3n,2}$ 3.8)	2.77	6.17, 5.97 ($^3J_{5,6}$ 5.1, $^3J_{5,4}$ 2.7, $^3J_{6,1}$ 3.0)	1.33, 1.22 ($^2J_{7s,7a}$ 7.8)	2.40–2.50	1.50–2.00 (15H, Ad), 2.40–2.38 (2H, CH_2Ad), 2.32 (4H, CH_2CH_2)
VIIf	2.95	2.20–2.30	1.70–1.80 ($^2J_{3x,3n}$ 11.4)	0.64 ($^3J_{3n,2}$ 3.2)	2.81	6.22, 6.04 ($^3J_{5,6}$ 5.4, $^3J_{5,4}$ 2.8, $^3J_{6,1}$ 3.0)	1.35, 1.27 ($^2J_{7s,7a}$ 7.8)	2.55–2.65	1.45–2.00 (15H, Ad), 2.50–2.67 (2H, CH_2Ad), 8.20–8.32 (2H, NH, OH)
VIIg	2.90	2.40	1.86 ($^2J_{3x,3n}$ 11.6)	0.58	2.80	6.22, 6.00	1.35, 1.23 ($^2J_{7s,7a}$ 8.1)	2.80–2.90	1.50–2.00 (15H, Ad), 3.35, 3.28 (2H, CH_2Ad), 7.90 (1H, NH), 7.25, 7.70 (4H, H_{arom})
VIIIa	2.74	1.48	1.14 ($^2J_{3x,3n}$ 12.0)	0.92 ($^3J_{3n,2}$ 4.0, $^3J_{3n,7s}$ 2.6)	2.82	6.00, 5.86 ($^3J_{5,6}$ 6.4, $^3J_{5,4}$ 2.6, $^3J_{6,1}$ 2.8)	1.35, 1.27 ($^2J_{7s,7a}$ 8.4)	2.90–3.15	1.50–2.00 (15H, Ad), 3.35 3.28 (2H, CH_2Ad), 8.00 8.34 (4H, H_{arom})
VIIIb	2.71	1.50–1.60	2.21	0.97	2.85	3.31, 3.29	1.24, 0.86	2.80–3.00	1.50–2.00 (15H, Ad), 2.80-3.00 (2H, CH_2Ad), 7.97 8.35 (4H, H_{arom})
IXd	2.81	2.11	1.75 ($^2J_{3x,3n}$ 12.0, $^3J_{3x,2}$ 9.2, $^3J_{3x,4}$ 3.8)	0.44 ($^3J_{3n,2}$ 3.6, $^3J_{3n,7s}$ 2.4)	2.85	6.09, 5.86 ($^3J_{5,6}$ 5.8, $^3J_{5,4}$ 2.9, $^3J_{6,1}$ 2.8)	1.36, 1.18 ($^2J_{7s,7a}$ 8.0)	2.70–3.00	1.50–2.00 (15H, Ad), 2.70-3.00 (2H, CH_2Ad), 6.21 (1H NH), 7.33, 7.77 (4H, H_{arom})
Xa	2.83	2.31	1.82 ($^2J_{3x,3n}$ 11.4, $^3J_{3x,2}$ 8.7)	0.54	2.92	6.20, 5.98 ($^3J_{5,6}$ 5.7, $^3J_{5,4}$ 2.7, $^3J_{6,1}$ 3.0)	1.44, 1.27 ($^2J_{7s,7a}$ 8.7)	2.80–3.00	1.40–2.00 (15H, Ad), 3.00-3.25 (2H, CH_2N), 7.96, 8.3((4H, H_{arom})

In the ^{1}H NMR spectrum of compound **VIIj** signals appeared in the regions 4.94 and 2.54, 2.42 ppm belonging to the proton of the methine group (H^x) neighboring to a hydroxy group, and to the protons of the methylene group (H^A, H^B) contiguous with the nitrogen. The area ratio of signals corresponding to the mentioned groups evidences that the epoxy group of the *p*-nitrophenyloxirane opens in keeping with Krasusky rule [19]; however alongside the main aminolysis product a side product is present in the reaction mixture whose respective signals in the ^{1}H NMR are observed at 4.64 and 3.62 ppm. The area ratio of signals (2:1) and their position suggest that the side product arises from the epoxy ring opening anti-Krasusky.

EXPERIMENTAL

IR spectra were measured on a spectrophotometer Specord 75-IR in the region 4000–400 cm^{-1} from thin

films or KBr pellets. ^{1}H NMR spectra were registered on spectrometers Varian VXR (operating frequencies 200 and 300 MHz) from solutions of compounds in deutero-chloriform or deuterodimethyl sulfoxide using TMS for internal reference. The spectra of compounds **IVa–IVe, Va, Vb, Vd, Ve, VIIa–VIIc, VIIe–VIIg, VIIIa, VIIIb, IXd**, and **Xa** are listed in Tables 1 and 2. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Silufol-60F_{254} plates, eluent ether, development in iodine vapor. Elemental analysis was carried out on a Karlo Erba analyzer.

Stereoisomeric bicyclo[2.2.1]hept-5-en-2-ylmethylamines (IIIa and IIIb) and *exo*-5,6-epoxybicyclo-[2.2.1]hept-*exo*-2-ylmethylamine (IIIc) were prepared as described in [8, 9], and their properties were consitent with the published data.

***N*-(Bicyclo[2.2.1]hept-5-en-*exo*-2-ylmethyl)-1-adamantanecarboxamide (IVa)**. To a stirred mixture of 2.20 g (17.8 mmol) of amine **IIIa** and 1.76 g (2.4 ml, 17.8 mmol) of triethylamine in 15 ml of chloroform was added dropwise a solution of 3.50 g (17.8 mmol) of 1-adamantanecarbonyl chloride in chloroform. The stirring at room temperature was continued till the completion of reaction (TLC monitoring). The reaction mixture was treated in succession with water, 5% hydrochloric acid solution, once more with water, then the organic layer was dried over anhydrous magnesium sulfate, the solvent was removed, and the reaction product was purified by recrystallization from an aqueous 2-propanol. Yield 70%, mp 180–181°C, R_f 0.31. IR spectrum, cm^{-1}: 3334, 3056, 1631, 1535, 1270, 712. Found, %: N 4.85. $C_{19}H_{27}NO$. Calculated, %: N 4.91.

***N*-(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-1-adamantanecarboxamide (IVb)** was prepared from amine **IIIb** by the above procedure. Yield 69%, mp 179–181°C [10], R_f 0.34. IR spectrum, cm^{-1}: 3430, 3026, 1622, 1526, 1243, 725.

***N*-(*exo*-5,6-Epoxybicyclo[2.2.1]hept-5-en-*exo*-2-ylmethyl)-1-adamantanecarboxamide (IVc)** was prepared by the above procedure from epoxyamine **IIIc**. Yield 55%, mp 96–98°C, R_f 0.75. IR spectrum, cm^{-1}: 3361, 3028, 1635, 1530, 1270, 1192, 851. Found, %: N 4.60. $C_{19}H_{27}NO_2$. Calculated, %: N 4.65.

***N,N*'-Bis(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)adamantane-1,3-dicarboxamide (IVd)** was prepared similarly from amine **IIIb** and 1,3-adamantanedicarbonyl chloride. Yield 64%, mp 200–202°C, R_f 0.37. IR spectrum, cm^{-1}: 3345, 3050, 1623, 1544, 1250, 730. Found, %: N 6.51. $C_{28}H_{38}N_2O_2$. Calculated, %: N 6.45.

***N,N*'-Bis(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)adamantane-1,3-diacetamide (IVe)** was prepared similarly from amine **IIIb** and 1,3-adamantanediacetic acid. Yield 72%, oily substance, R_f 0.35. IR spectrum, cm^{-1}: 3345, 3050, 1635, 1530, 1270, 1192, 851. Found, %: N 6.14. $C_{30}H_{42}N_2O_2$. Calculated, %: N 6.06.

***N,N*'-Dibenzyl-1,3-adamantanedicarboxamide (IVf)** was prepared analogously. Yield 70%, mp 151–152°C, R_f 0.33. ^{1}H NMR spectrum, δ, ppm: 1.84 m, 2.11 m, 2.25 m, 4.43 d, 7.29 m. Found, %: N 6.90. $C_{26}H_{30}N_2O_2$. Calculated, %: N 6.97.

***N*-(1-Adamantylmethyl)bicyclo[2.2.1]hept-5-en-*exo*-2-ylmethylamine (Va)**. To a stirred dispersion of 0.40 g (10.5 mmol) of lithium aluminum hydride in 10 ml of anhydrous ethyl ether was added dropwise a solution of 1.40 g (5.0 mmol) of amide **IVa** in 10 ml of anhydrous ether. The mixture was stirred for 8 h at reflux (TLC monitoring). The excess lithium aluminum hydride was decomposed with aqueous ether and then with ice water. The organic layer was separated, dried over anhydrous magnesium sulfate, the solvent was removed. Yield 95%, oily substance, R_f 0.92. IR spectrum, cm^{-1}: 3391, 3065, 1571, 712. Found, %: N 5.24. $C_{19}H_{29}N$. Calculated, %: N 5.17. Hydrochloride **VIa** of amine **Va** was prepared by passing a flow of dry hydrogen chloride through an ether solution of the amine. Yield 70%, mp 230°C (decomp.). IR spectrum, cm^{-1}: 3071, 2722, 1440, 730.

***N*-(1-Adamantylmethyl)bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethylamine (Vb)** was prepared by the above procedure from amide **IVb**. Yield 94%, oily substance, R_f 0.88. IR spectrum, cm^{-1}: 3348, 3040, 1568, 718. Found, %: N 5.25. $C_{19}H_{29}N$. Calculated, %: N 5.17. Hydrochloride **VIb** was obtained in 74% yield, mp 230°C (decomp.). IR spectrum, cm^{-1}: 3061, 2725, 1440, 720.

***N*-(1-Adamantylmethyl)-*exo*-5,6-epoxybicyclo-[2.2.1]hept-*exo*-2-ylmethylamine (Vc)** was obtained analogously from amide **IVc**. Yield 87%, oily substance, R_f 0.96. IR spectrum, cm^{-1}: 3368, 3030, 1551, 856. Found, %: N 4.93. $C_{19}H_{29}NO$. Calculated, %: N 4.87. Hydrochloride (**VIb**) was obtained in 71% yield, mp 191–193°C. IR spectrum, cm^{-1}: 3028, 2703, 1440, 855.

***N,N*'-Bis(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-1,3-adamantanedimethylamine (Vd)** was obtained analogously by reduction of amide **IVd**. Yield 97%, oily substance, R_f 0.28. IR spectrum, cm^{-1}: 3410, 3041, 1573, 720. Found, %: N 6.80. $C_{28}H_{42}N_2$. Calculated, %: N 6.89. Hydrochloride **VId** was obtained in 80% yield, mp 185–187°C. IR spectrum, cm^{-1}: 3030, 2700, 1440, 720.

***N,N'*-Bis(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-1,3-adamantanediethylamine (Ve)**. To a stirred dispersion of 0.39 g (10.3 mmol) of lithium aluminum hydride in 10 ml of anhydrous ethyl ether was added dropwise a solution of 1.20 g (2.6 mmol) of amide **IVe** in 10 ml of anhydrous ether, and the mixture was stirred for 10 h at room temperature (TLC monitoring). The excess lithium aluminum hydride was decomposed with aqueous ether and then with ice water. The organic layer was separated, dried over anhydrous magnesium sulfate, the solvent was removed. Yield 94%, oily substance, R_f 0.24. IR spectrum, cm^{-1}: 3315, 3062, 1561, 730. Found, %: N 6.52. $C_{30}H_{46}N_2$. Calculated, %: N 6.45. Hydrochloride **VIe** was obtained in 78% yield, mp 196–198°C. IR spectrum, cm^{-1}: 3064, 2720, 1452, 731.

***N,N'*-Dibenzyl-1,3-adamantanedimethylamine (Vf)** was similarly prepared from amide **IVf**. Yield 98%, oily substance, R_f 0.23. IR spectrum, cm^{-1}: 3400, 3028, 1573, 703. ^{1}H NMR spectrum, δ, ppm: 1.42 m, 1.64 m, 2.00 m, 2.25 s, 3.71 s, 7.26 m. Found, %: N 7.42. $C_{26}H_{34}N_2$. Calculated, %: N 7.49. Hydrochloride **VIf** was obtained in 83% yield, mp 202–204°C. IR spectrum, cm^{-1}: 2700, 1440, 705.

***N*-(1-Adamantylmethyl)-*N*-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*p*-nitrophenylsulfonamide (VIIa)**. To a stirred mixture of 0.20 g (0.74 mmol) of amine **Vb** and 0.006 g (0.06 ml, 0.74 mmol) of pyridine in 8 ml of anhydrous chloroform was added dropwise at room temperature a solution of 0.17 g (0.74 mmol) of *p*-nitrobenzenesulfonyl chloride in 6 ml of chloroform, the mixture was heated to 60°C and stirred at this temperature for 4 h. The completion of the process was fixed by TLC, then the reaction mixture was treated in succession with water, 5% solution of hydrochloric acid, again with water. Then the organic layer was separated, dried over anhydrous magnesium sulfate, the solvent was removed, and the reaction product was purified by recrystallization from an aqueous 2-propanol. Yield 84%, mp 145–146°C, R_f 0.82. IR spectrum, cm^{-1}: 3051, 1530, 1370, 1352, 1250, 1190, 730. Found, %: N 6.05. $C_{25}H_{32}N_2O_4S$. Calculated, %: N 6.14.

***N*-(1-Adamantylmethyl)-N-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*p*-chlorophenylsulfonamide (VIIb)** was likewise prepared from amine **Vb** and *p*-chlorobenzenesulfonyl chloride. Yield 45%, mp 105–106°C, R_f 0.76. IR spectrum, cm^{-1}: 3050, 1583, 1341, 1180, 732. Found, %: N 3.07. $C_{25}H_{32}ClNO_2S$. Calculated, %: N 3.14.

***N*-(1-Adamantylmethyl)-N-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*p*-toluenesulfonamide (VIIc)** was likewise prepared from amine **Vb** and *p*-toluenesulfonyl chloride. Yield 61%, oily substance, R_f 0.79. Found, %: N 3.37. $C_{26}H_{35}NO_2S$. Calculated, %: N 3.29.

***N*-(1-Adamantylmethyl)-*N*-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*p*-nitrobenzamide (VIId)**. To a stirred mixture of 0.20 g (0.7 mmol) of amine **Vb** and 0.006 g (0.06 ml, 0.74 mmol) of pyridine in 8 ml of anhydrous chloroform was added dropwise at room temperature a solution of 0.15 g (0.7 mmol) of *p*-nitrobenzoyl chloride in 6 ml of chloroform, the mixture was heated to 60°C and stirred at this temperature for 4 h. The completion of the process was fixed by TLC, then the reaction mixture was treated in succession with water, 5% solution of hydrochloric acid, again with water. Then the organic layer was separated, dried over anhydrous magnesium sulfate, the solvent was removed, and the reaction product was recrystallized from a mixture of 2-propanol and water. Yield of **VIId** 78%, mp 135–136°C, R_f 0.81. IR spectrum, cm^{-1}: 3057, 1635, 1527, 1350, 1280, 720. Found, %: N 6.60. $C_{26}H_{32}N_2O_3$. Calculated, %: N 6.67.

3-[*N*-(1-Adamantylmethyl)-*N*-bicyclo[2.2.1]-hept-5-en-*endo*-2-ylmethyl]carbamoylpropionic acid (VIIe). To a solution of 0.15 g (0.5 mmol) of amine **Vb** in 5 ml of ethyl acetate was added a solution of 0.05 g (0.5 mmol) of succinic anhydride, and the mixture was heated for a short time (15 min) at 40–50°C. On cooling the separated precipitate was filtered off, washed with ethyl acetate, the reaction product was recrystallized from hot ethyl acetate. Yield of amidoacid 69%, mp 139–140°C, R_f 0.18. IR spectrum, cm^{-1}: 3412, 3071, 1712, 1645, 1552, 721. Found, %: N 3.71. $C_{23}H_{33}NO_3$. Calculated, %: N 3.77.

***endo*-3-[*N*-(1-Adamantylmethyl)-*N*-(bicyclo-[2.2.1]hept-5-en-*endo*-2-ylmethyl)carbamoyl]-bicyclo[2.2.1]hept-5-en-*endo*-2-carboxylic acid (VIIf)**. To a solution of 0.15 g (0.5 mmol) of amine **Vb** in 5 ml of anhydrous benzene was added a solution of 0.90 g (0.5 mmol) of endic anhydride in the same solvent, and the mixture was heated for a short time (15 min) at 40–50°C. On cooling the separated precipitate was filtered off, washed with cool benzene, the reaction product was recrystallized from hot benzene. Yield 63%, mp 132–133°C, R_f 0.25. IR spectrum, cm^{-1}: 3060, 1740, 1700, 1651, 1550, 1270, 740. Found, %: N 3.29. $C_{28}H_{37}NO_3$. Calculated, %: N 3.22.

N-(1-Adamantylmethyl)-N-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*N'*-*p*-toluenesulfonylcarbamide (VIIg). To a solution of 0.15 g (0.5 mmol) of amine **Vb**

in 3 ml of benzene was added at room temperature 0.10 g (0.5 mmol, 0.1 ml) of *p*-tosyl isocyanate; the end of reaction was checked by TLC. The separated precipitate was filtered off, washed on the filter with benzene, and dried. The reaction product was recrystal-lized from the benzene–hexane mixture. Yield 76%, mp 93–95°C, R_f 0.42. IR spectrum, cm^{-1}: 3412, 3068, 1645, 1570, 1351, 1270, 730. Found, %: N 6.07. $C_{27}H_{36}N_2O_3S$. Calculated, %: N 5.98.

***N*-(1-Adamantylmethyl)-N-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*N*'-*m*-tolylcarbamide (VIIh)** was prepared in the same fashion from amine **Vb** and *m*-tolyl isocyanate. Yield 61%, oily substance, R_f 0.81. IR spectrum, cm^{-1}: 3345, 3065, 1640, 1551, 1240, 730. Found, %: N 7.03. $C_{27}H_{36}N_2O$. Calculated, %: N 6.93.

***N*-(1-Adamantylmethyl)-N-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*N*'-phenylthiocarbamide (VIIi)** was prepared in the same fashion from amine **Vb** and phenyl isothiocyanate. Yield 72%, oily substance, R_f 0.88. IR spectrum, cm^{-1}: 3310, 3067, 1540, 1310, 1110, 732. Found, %: N 6.98. $C_{26}H_{33}N_2S$. Calculated, %: N 6.91.

2-[*N*-(1-Adamantylmethyl)-*N*-(bicyclo[2.2.1]-hept-5-en-*endo*-2-ylmethyl)aminO]-1-(*p*-nitrophenyl)-1-ethanol (VIIj). To a solution of 0.15 g (0.5 mmol) of amine **Vb** in 3 ml of 2-propanol was added at room temperature a solution of 0.10 g (0.5 mmol) of *p*-nitrophenyloxirane in the same solvent; the end of reaction was checked by TLC. The solvent was removed, the mixture of products was subjected to column chromatography on silica gel (eluent ether). Yield 63%, oily substance, R_f 0.93. IR spectrum, cm^{-1}: 3395, 3070, 1610, 1534, 1351, 1160, 730. Found, %: N 6.70. $C_{27}H_{36}N_2O_3$. Calculated, %: N 6.61.

***N*-(1-Adamantylmethyl)-*N*-(bicyclo[2.2.1]hept-5-*exo*-2-methyl)-*n*-nitrophenylsulfonamide (VIIIa)**. To a stirred mixture of 0.20 g (0.74mmol) of amine **Va** and 0.006 g (0.06 ml, 0.74 mmol) of pyridine in 8 ml of anhydrous chloroform was added dropwise at room temperature a solution of 0.17 g (0.74 mmol) of *p*-nitrobenzenesulfonyl chloride in 6 ml of chloroform, the mixture was heated to 60°C and stirred at this temperature for 4 h. The completion of the process was fixed by TLC, then the reaction mixture was subjected to commom workup. The reaction product was purified by column chromatography on silica gel (eluent ether). Yield 72%, oily substance, R_f 0.90. Found, %: N 6.08. $C_{25}H_{32}N_2O_4S$. Calculated, %: N 6.14.

***N*-(1-Adamantylmethyl)-N-(*exo*-5,6-epoxybicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*p*-nitrophenylsulfonamide (VIIIb)** was prepared from amine **Vc** and *p*-nitrobenzenesulfonyl chloride along the procedure described for compound **VIIIa**. Yield 50%, mp 156–158°C, R_f 0.94. IR spectrum, cm^{-1}: 3025, 1527, 1340, 1168, 1115, 858. Parameters of ^{1}H NMR spectrum are given in Table 2. Found, %: N 5.99. $C_{25}H_{32}N_2O_5S$. Calculated, %: N 5.93.

***N*-(1-Adamantylmethyl)-*N*-(*exo*-5,6-epoxybicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-*N*'-*p*-toluenesulfonylcarbamide (VIIIc)** was prepared from amine **Vc** and *p*-tosyl isocyanate along the procedure described for compound **VIIg**. Yield 80%, mp 92–93°C, R_f 0.68. IR spectrum, cm^{-1}: 3361, 1653, 1530, 1310, 1165, 859. Found, %: N 5.70. $C_{27}H_{36}N_2O_4S$. Calculated, %: N 5.79.

1,3-Bis[*N*-(*p*-nitrophenylsulfonyl)-*N*-(bicyclo-[2.2.1]hept-5-en-*endo*-2-ylmethyl)amino-methyl]-adamantane (IXa) was prepared along the procedure described for compound **VIIa** from amine **Vd** and *p*-nitrobenzenesulfonyl chloride. Yield 63%, oily substance, R_f 0.91. IR spectrum, cm^{-1}: 3056, 1537, 1370, 1349, 1190, 731. Found, %: N 7.08. $C_{40}H_{50}N_4O_8S_2$. Calculated, %: N 7.20.

1,3-Bis[N-(*p*-nitrobenzoyl)-*N*-(bicyclo[2.2.1]-hept-5-en-*endo*-2-ylmethyl)aminomethyl]-adamantane (IXb) was obtained similarly to amide **VIId** from amine **Vd** and *p*-nitrobenzoyl chloride. Yield 69%, oily substance, R_f 0.92. IR spectrum, cm^{-1}: 3070, 1613, 1531, 1375, 731. Found, %: N 7.82. $C_{42}H_{50}N_4O_6$. Calculated, %: N 7.93.

1,3-Bis[*N*-(3-carboxypropionyl)-*N*-(bicyclo-[2.2.1]hept-5-en-*endo*-2-ylmethyl)aminomethyl]-adamantane (IXc) was prepared from 0.20 g (0.5 mmol) of amine **Vd** in 5 ml of ethyl acetate and 0.10 g (1.0 mmol) of succinic anhydride by the procedure described for amidOacid **VIIIe**. The reaction product was purified by column chromatography on silica gel (eluent ether).. Yield 58%, oily substance, R_f 0.65. IR spectrum, cm^{-1}: 3390, 1712, 1631, 1555, 1290, 730. Found, %: N 4.72. $C_{36}H_{52}N_2O_6$. Calculated, %: N 4.61.

1,3-Bis[*N*-(*p*-toluenesulfonylcarbamoyl)-*N*-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)amino-methyl]adamantane (IXd) was obtained from amine **Vd** and and *p*-tosyl isocyanate along the procedure described for compound **VIIg**. Yield 63%, mp 104–106°C, R_f 0.56. Found, %: N 7.13. $C_{44}H_{56}N_4O_6S_2$. Calculated, %: N 7.00.

1,3-Bis[*N*-(*m*-toluenecarbamoyl)-*N*-(bicyclo-[2.2.1]hept-5-en-*endo*-2-ylmethyl)aminomethyl]-

adamantane (IXe) was obtained from amine **Vd** and *m*-tosyl isocyanate along the procedure described for compound **VIIg**. The product was purified by passing through a column packed with silica gel (eluent ether). Yield 51%, oily substance, R_f 0.61. IR spectrum, cm^{-1}: 3351, 3070, 1642, 1556, 1290, 731. Found, %: N 8.21. $C_{44}H_{56}N_4O_2$. Calculated, %: N 8.33.

1,3-Bis[*N*-(*p*-nitrophenylsulfonyl)-*N*-(bicyclo-[2.2.1]hept-5-en-*endo*-2-ylmethyl)-(2-aminoethyl)]-adamantane (Xa). To a stirred mixture of 0.25 g (0.6 mmol) of amine **Ve** and 0.11 g (0.16 ml, 1.1 mmol) of triethylamine in 8 ml of dry chloroform was added dropwise a solution of 0.26 g (1.1 mmol) of *p*-nitrobenzenesulfonyl chloride in 6 ml of chloroform. The mixture was stirred at room temperature for 7 h. The end of the process was checked by TLC. After the common workup the reaction product was purified by passing through a column packed with silica gel (eluent ether). Yield 57%, oily substance, R_f 0.76. IR spectrum, cm^{-1}: 3061, 1542, 1370, 1344, 1186, 730. Found, %: N 6.78. $C_{42}H_{54}N_4O_8S_2$. Calculated, %: N 6.91.

1,3-Bis[*N*-(*p*-toluenesulfonylcarbamoyl)-*N*-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-(2-aminoethyl)]adamantane (Xb) was obtained from amine **Ve** and and *p*-tosyl isocyanate along the procedure described for compound **VIIg**. Yield 71%, mp 87–88°C, R_f 0.69. IR spectrum, cm^{-1}: 3392, 3236, 3065, 1641, 1556, 1335, 1270, 1161, 730. Found, %: N 6.85. $C_{46}H_{60}N_4O_6S_2$. Calculated, %: N 6.73.

1,3-Bis[*N*-(*p*-nitrobenzenesulfonyl)-*N*-(benzyl)-aminomethyl]adamantane (XIa) was obtained at room temperature from amine **Vf** and *n*-nitrobenzenesulfonyl chloride along the procedure described for compound **Xa**. Yield 87%, mp 160–162°C, R_f 0.56. IR spectrum, cm^{-1}: 3043 1534, 1360, 1180, 1138. Found, %: N 7.40. $C_{38}H_{42}N_4O_8S_2$. Calculated, %: N 7.51.

1,3-Bis[*N*-(*p*-toluenesulfonylcarbamoyl)-*N*-(benzyl)aminomethyl]adamantane (XIb) was obtained in the same way as compound **Vg** from amine **Vf** and *p*-tosyl isocyanate. Yield 75%, mp 112–114°C, R_f 0.52. IR spectrum, cm^{-1}: 3381, 1647, 1605, 1570, 1356, 1276. Found, %: N 7.32. $C_{42}H_{50}N_4O_6S_2$. Calculated, %: N 7.27.

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