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Derivatives of *exo*-5-Aminomethyl-*endo*-5-methylbicyclo-[2.2.1]hept-2-ene and *exo*-5-Aminomethyl-*endo*-5-methyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane

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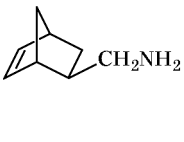
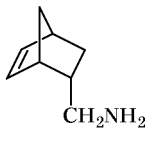
Abstract—*exo*-5-Aminomethyl-*endo*-5-methylbicyclo[2.2.1]hept-2-ene and its 2,3-epoxy derivative were synthesized, and their geometric parameters and conformational properties, in particular the barriers to rotation of the aminomethyl fragment about the exocyclic C^5-C bond, were studied by the molecular-mechanics method (MMX) and compared with those found for structurally related *exo*-5-aminomethylbicyclo[2.2.1]hept-2-ene. The title compounds were brought into reactions with electrophilic reagents: arenesulfonyl chlorides, isocyanates, and isothiocyanates.

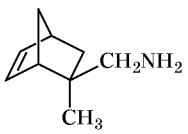
Increased interest in the chemistry of amines, sulfonamides, carboxamides, and urea derivatives containing polycyclic fragments is explained by a wide spectrum of valuable pharmacological properties intrinsic to these compounds [1]. New efficient antidiabetic drugs [2] and thromboxane antagonists [3] were found among derivatives of bicyclic amines. Arenesulfonamides derived from stereoisomeric *exo*- and *endo*-5-aminomethylbicyclo[2.2.1]hept-2-enes **Ia** and **IIb** were shown to exhibit neurotropic and antiphlogistic activity [4, 5]. The kind and magnitude of biological effect strongly depend on both orientation of substituent (*exo* or *endo*) in the bicyclic fragment and nature of substituent in the benzene ring [6]. Taking into account that the contributions of substituents in different positions of the norbornene fragment to biological activity were not studied up to now, we synthesized derivatives of *exo*-5-aminomethyl-*endo*-5-methylbicyclo[2.2.1]hept-2-ene (**II**) (which was described previously [7]) and its 2,3-epoxy analog **III** which are structurally related to amine **Ia**.



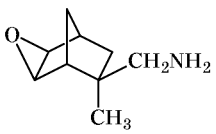
Ia



Ib



II



III

The stereoselective Diels–Alder reaction of cyclopentadiene with methacrylonitrile [8] gave nitrile **IV** as a single stereoisomer. Its properties coincided with those of a sample described previously. The IR spectrum of **IV** contained absorption bands at 2224 and 1564 cm^{-1}, corresponding to stretching vibrations of the cyano group and C=C bond of the norbornene fragment [9]. By reduction of **IV** with lithium aluminum hydride in dry ether we obtained amine **II** (Scheme 1) which showed in the IR spectrum bands typical of stretching vibrations of N–H bond (3348 and 3274 cm^{-1}) and stretching (3042 cm^{-1}) and bending vibrations (726 cm^{-1}) of =C–H bond [4, 5].

Compound **III** was synthesized by oxidation of nitrile **IV** with peroxyphthalic acid, followed by reduction of epoxy nitrile **V** with lithium aluminum hydride under the same conditions as in the synthesis of **II**. The IR spectra of epoxy derivatives **III** and **V** contained strong absorption bands in the region 850–848 cm^{-1}, corresponding to vibrations of the C–O bonds in molecules of epoxynorbornanes, and in the region 3030–3020 cm^{-1}, due to C–H bonds in the three-membered rings [4, 9]. The cyano and aminomethyl groups in compounds **III** and **V** give rise to IR bands at 2227 and 3300–3200 cm^{-1}, respectively.

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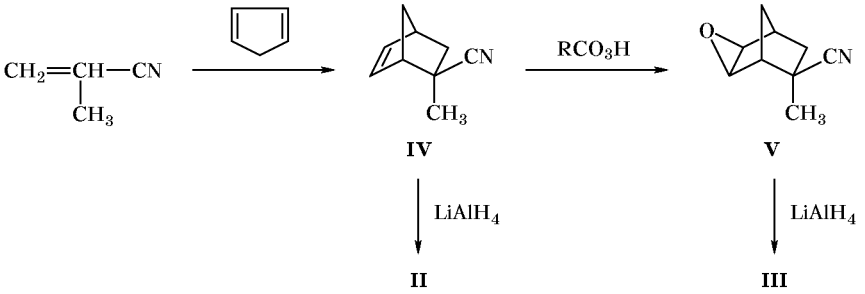
Scheme 1.



The ^{1}H NMR spectral parameters of **V** indicate the presence of an oxirane ring (δ 3.15 ppm) and methyl group (δ 1.45 ppm).

The structure of amines **II** and **III** was not studied previously. Structurally related *exo*-amine **Ia** was examined in [10] by the molecular-mechanics method (MMX) [11]; these results were used for comparison with those obtained in the present work for amines **II** and **III**. Amines **I**–**III** possess a conformationally labile aminomethyl moiety which suffers an influence of the bulky carbon skeleton. Conformation of the molecule can strongly affect the chemical and pharmacological properties of the amines. Figure shows the change in the total steric energy (TSE) on variation of the torsion angle $C^4C^5C^8N$ due to rotation of the aminomethyl fragment about the bond linking the carbon atoms of the aminomethyl group and bicyclic skeleton. There are three minima on the plots, which correspond to favorable conformations of molecules **Ia** and **II**. The energy parameters of different conformations of molecules **Ia**, **II**, and **III** and the corresponding rotation barriers are given in Table 1. It is seen that the barrier to rotation about the C^5-C^8 bond considerably increases on introduction of a methyl group to C^5 and that conformer **B** is the most favorable for all the examined amines.

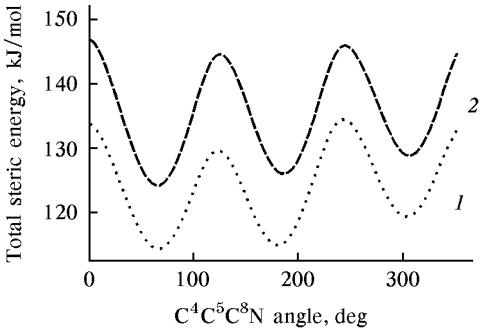
We compared the strain energies and geometric parameters of the most stable conformers of amines **Ia**, **II**, and **III** (Table 2). The presence of a methyl group on C^5 strongly increases the strain energy due mainly to the contributions of torsion strain and van der Waals interactions. According to the calculations, the cyclohexane ring (which is a base fragment of the bicyclic skeleton) becomes more flattened when the methyl group occupies the *endo*-position (the $C^3C^4C^5$ angle increases, and the $C^3C^4C^7$ angle decreases. Decrease of the $C^4C^5C^8$ angle under the influence of the methyl group should also be noted.

The transformation of the $C^2=C^3$ bond into oxirane ring (compound **III**) is accompanied by considerable change of the carbon skeleton structure, as compared to amine **II**. In particular, additional flattening of the carbon skeleton occurs (the $C^3C^4C^5$ angle increases), and the methylene bridge declines from the oxirane ring (the $C^3C^4C^7$ angle increases, and the $C^5C^4C^7$ angle decreases).

The reactivity of amines toward electrophiles is determined by their nucleophilicity. The nucleophilic

Table 1. Torsion angles $C^4C^5C^8N$ (deg) in stable conformers **A**, **B**, and **C** of amines **Ia**, **II**, and **III** and their energy parameters and rotation barriers (kJ/mol)

Compound no.	Conformer	$C^4C^5C^8N$ angle	Total steric energy	Heat of formation	Rotation barrier **A**–**B**–**C**–**A**
Ia	**A**	62.4	114.68	82.59	17.30
	B	–178.3	114.06	81.92	23.07
	C	–58.1	120.29	88.16	13.95
II	**A**	63.1	124.93	56.36	22.18
	B	–176.6	124.68	56.15	24.27
	C	–54.1	129.82	61.29	18.03
III	**A**	60.8	161.08	–54.68	21.51
	B	–175.5	161.46	–54.31	22.97
	C	–56.2	167.67	–48.07	15.94



Plots of the total steric energy of conformers of compounds (*1*) **Ia** and (*2*) **II** versus the torsional angle $C^4C^5C^8N$.

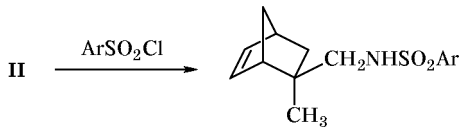
properties of amines of the norbornene series was estimated previously by semiempirical quantum-chemical calculations [7]. The proton affinities of compounds **Ia**, **II**, and **III** are 691.15, 702.16, and 684.84 kJ/mol, respectively [7]. Variation of this parameter corresponds to change of electron density on the amino group nitrogen atom due to electron-donor effect of the methyl group and electron-acceptor effect of the oxirane oxygen atom.

Amines **II** and **III** were brought into reactions with some electrophilic reagents: arenesulfonyl chlorides, isocyanates, and isothiocyanates. The reactions of amine **II** with a number of arenesulfonyl chlorides gave sulfonamides **VI**–**X** (Scheme 2). The reactions were carried out with equimolar amounts of the reactants under vigorous stirring in a two-phase system (ether–water) in the presence of alkali.

Table 2. Calculated energy and structure parameters of compounds **Ia**, **II**, and **III**

Parameter	**Ia**	**II**	**III**
Strain energy E_S, kJ/mol	98.63	106.36	210.33
C^2-C^3 bond length, Å	1.338	1.338	1.514
Bond angle, deg			
$C^3C^4C^5$	106.2	107.9	109.0
$C^2C^1C^6$	102.2	102.6	101.0
$C^5C^4C^7$	98.5	97.8	104.1
$C^3C^4C^7$	107.8	108.2	107.7
$C^1C^7C^4$	93.4	93.2	91.7
$C^4C^5C^6$	102.5	101.5	101.1
$C^4C^5C^8$	112.8	110.4	110.7
Torsion angle, deg			
$C^4C^5C^6C^1$	–3.1	–2.1	–0.9
$C^4C^3C^2C^1$	–0.5	–1.0	–2.6

Scheme 2.



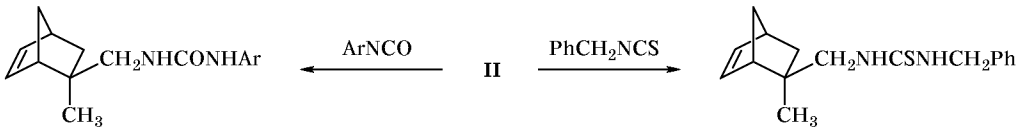
VI–**X**

VI, Ar = 4-$NO_2C_6H_4$; **VII**, Ar = 2,4-$(NO_2)_2C_6H_3$; **VIII**, Ar = 2-CH_3-4-$NO_2C_6H_3$; **IX**, Ar = 2-CH_3-4-FC_6H_3; **X**, Ar = 4-ClC_6H_4.

Some ureas and thioureas derived from amine **II** were described in [7]. These include products of reactions with *m*-chlorophenyl isocyanate, cyclohexyl isocyanate, phenyl isothiocyanate, and α-naphthyl isothiocyanate. In the present work we examined the reactions of **II** with phenyl isocyanate, methyl isocyanate, and benzyl isothiocyanate (Scheme 3). Epoxy amine **III** was converted into sulfonylurea **XIV** by reaction with *p*-tolylsulfonyl isocyanate in benzene (Scheme 4). Table 3 contains the yields, melting points, R_f values, IR spectra, and elemental analyses of compounds **VI**–**XIV**. In the IR spectra of sulfonamides **VI**–**X** and **XIV** we observed absorption bands in the regions 1350–1310 and 1180–1160 cm^{-1} due to stretching vibrations of the SO_2 group. Stretching vibration bands of the N–H bond appeared in the region 3370–3300 cm^{-1}. The IR spectra of ureas contain bands at 1640–1620, 1565–1555, and 1245–1225 cm^{-1}, belonging to stretching vibrations of the carbonyl group, bending vibrations of the N–H bond, and stretching vibrations of the C–N bond. It was difficult to assign absorption bands in the region 3080–3040 cm^{-1} owing to the presence of two unsaturated fragments, strained double bond and aromatic ring. Informative absorption bands are those observed at 725–710 cm^{-1}; they were assigned to bending vibrations of the =C–H bonds in the norbornene fragment. The IR spectrum of epoxy derivative **XIV** lacks absorption at 3040 cm^{-1}, but bands at 3020 and 3080–3060 cm^{-1} are present. The first of these belongs to the C–H bonds of the oxirane ring. However, the most characteristic band is that corresponding to stretching vibrations of the oxirane C–O bond, which appears at 857 cm^{-1}. Also, bands at 3380, 3280, 1650, 1600, 1540, 1340, 1230, and 1160 cm^{-1} were present, which belong to vibrations of the urea and sulfonyl fragments.

Table 4 gives the ^1H NMR spectral parameters of sulfonamide **VI**; the data for known *N*-(*m*-chlorophenylcarbamoyl)-*exo*-5-aminomethyl-*endo*-5-methylbicyclo[2.2.1]hept-2-ene (**XV**) [7] and the closest

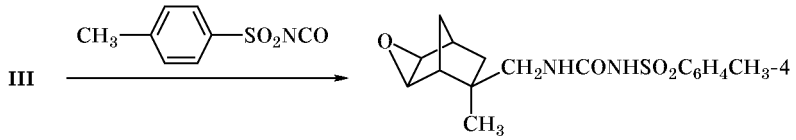
Scheme 3.



XI, XII **XIII**

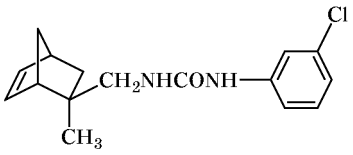
XI, Ar = C_6H_5; **XII**, Ar = 2,2,4-$(CH_3)_3C_6H_2$.

Scheme 4.

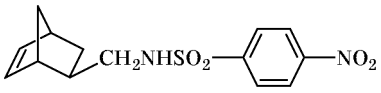


XIV

analog of **VI** containing no methyl group, *N*-(*p*-nitrophenylsulfonyl)-*exo*-2-aminomethylbicyclo[2.2.1]-hept-2-ene (**XVI**) [4], are also given for comparison.



XV



XVI

Compounds **VI** and **XV** showed in the ^{1}H NMR spectra resonance signals from protons at the double bond (δ 6.00–6.13 ppm) and methyl protons (δ 0.98 and 0.84 ppm). The signals from protons at C^8 are anisochronous, for the atoms neighboring to the chiral C^5 center are diastereotopic. A considerable difference in the chemical shifts of 1-H and 4-H is likely to result from the magnetically anisotropic effect of the exocyclic C^5-C^8 bond, which leads to shielding of 4-H (the C^4-H bond is parallel to C^5-C^8, and these bonds are spatially close to each other). The signals corresponding to protons of the methylene bridge (*syn*-7-H and *anti*-7-H) were assigned, taking into account additional splitting of one of these (upfield) due to coupling with *endo*-6-H, J = 2.2 and 2.5 Hz, respectively (*W*-coupling).

Analysis of the ^{1}H NMR spectra of compounds **VI** and **XVI** shows that the presence of the angular methyl group on C^5 leads to displacement of the *exo*-6-H and *endo*-6-H signals owing to anisotropic effect of the exocyclic *endo*-C^5-CH_3 bond. The same factor is likely to be responsible for increased nonequivalence of 2-H and 3-H in molecule **VI**, as compared to sulfonamide **XVI**.

We also examined pharmacological properties of *exo*-5-(*p*-nitrophenylsulfonylaminomethyl)-*endo*-5-methylbicyclo[2.2.1]hept-2-ene (**VI**) and compared its activity with that of analog **XVI** [4] which has no 5-methyl group. The results suggest similar mechanisms of the neurotropic activity of these compounds.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer in the range from 4000 to 400 cm^{-1}; samples were prepared as KBr pellets. The ^{1}H NMR spectra were obtained on a Varian VXR-300 instrument from solutions in $CDCl_3$ or DMSO-d_6 using HMDS or TMS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates with ether as eluent; chromatograms were developed with iodine vapor.

endo-5-Methylbicyclo[2.2.1]hept-2-ene-*exo*-5-carbonitrile (**IV**) was synthesized by the procedure reported in [8]. Yield 54%, bp 95–96°C (22 mm), mp 55–56°C; published data [8]: mp 47–49°C. IR spectrum, ν, cm^{-1}: 2224, 1564.

***exo*-2,3-Epoxy-*endo*-5-methylbicyclo[2.2.1]-heptane-*exo*-5-carbonitrile (V).** To a mixture of 2.98 g (0.02 mol) of compound **IV**, 4.5 g of acetic anhydride, and 4 g of sodium hydrogen carbonate in 10 ml of diethyl ether we added dropwise with stirring 1.5 g of 90% hydrogen peroxide, maintaining the temperature at 25–30°C. When the reaction was complete (TLC), the mixture was neutralized with

Table 3. Yields, melting points, R_f values, IR spectra, and elemental analyses of compounds **VI**–**XIV**

Comp. no.	Yield, %	mp, °C	R_f	IR spectrum, ν, cm^{-1}	Found, %			Formula	Calculated, %		
					C	H	N		C	H	N
VI	75.8	116–117.5	0.49	3372, 3040, 1624, 1450, 1350, 1182, 852, 724	56.01	5.57	8.68	$C_{15}H_{18}N_2O_4S$	55.88	5.63	8.69
VII	71.8	111–112	0.66	3348, 3029, 1570, 1348, 1151, 714	50.05	4.75	11.50	$C_{15}H_{17}N_3O_6S$	49.04	4.67	11.44
VIII	69.1	101.5–103	0.18	3345, 3030, 1560, 1345, 1149, 718	57.15	6.01	8.38	$C_{16}H_{20}N_2O_4S$	57.12	5.94	8.33
IX	60.5	113–115	0.52	3340, 3029, 1555, 1334, 1150, 712	62.18	6.59	4.30	$C_{16}H_{20}FNO_2S$	62.11	6.52	4.55
X	84.6	146–147	0.53	3350, 3065, 1570, 1320, 1160, 725	57.79	5.90	4.53	$C_{15}H_{18}ClNO_2S$	57.77	5.82	4.49
XI	63.5	181–182	0.90	3300, 3040, 1625, 1600, 1560, 1230, 721	74.90	7.95	10.73	$C_{16}H_{20}N_2O$	74.96	7.86	10.93
XII	70.1	240–242	0.48	3310, 3050, 1630, 1562, 1241, 719	76.49	8.65	9.48	$C_{19}H_{26}N_2O$	76.47	8.78	9.39
XIII	75.9	160–162	0.49	3298, 3055, 1666, 1510, 1330, 1230, 712	71.28	7.71	9.75	$C_{17}H_{22}N_2S$	71.31	7.75	9.79
XIV	73.6	98–100	0.59	3380, 3280, 1650, 1600, 1540, 1340, 1230, 1160	58.37	6.37	8.06	$C_{17}H_{22}N_2O_4S$	58.29	6.29	8.00

a saturated solution of sodium hydrogen carbonate, the organic layer was separated, the aqueous layer was washed with ether, and the organic phases were combined, dried, and evaporated. Yield 90%, mp 130–132°C. IR spectrum, ν, cm^{-1}: 3035, 2227, 848. The data were consistent with those given in [12].

exo-5-Aminomethyl-*endo*-5-methylbicyclo[2.2.1]-hept-2-ene (**II**) was synthesized by the procedure described in [7]. Yield 71%, bp 85–87°C (30 mm). IR spectrum, ν, cm^{-1}: 3348, 3274, 3042, 1568, 1252, 726. The data correspond to those given in [7].

***exo*-5-Aminomethyl-*exo*-2,3-epoxy-*endo*-5-methylbicyclo[2.2.1]heptane (III)** was prepared by analogy to amine **II** [7], by reduction of epoxy nitrile **V** with lithium aluminum hydride in dry ether. Yield 76%, bp 73–75°C (4 mm). IR spectrum, ν, cm^{-1}: 3322, 3260, 3058, 1560, 1220, 854, 712. Found, %: N 8.95. $C_9H_{15}NO$. Calculated, %: N 9.15.

exo*-5-(Arylsulfonylaminomethyl)-*endo*-5-methylbicyclo[2.2.1]hept-2-enes VI–X (general procedure***).** A solution of 0.01 mol of appropriate sulfonyl chloride in 10 ml of ether was added dropwise with stirring to a mixture of 0.14 g (0.01 mol) of amine **II**, 10 ml of ether, and 2 ml of 20% aqueous sodium hydroxide. When the reaction was complete (TLC), the organic layer was separated, dried over calcined magnesium sulfate, and evaporated. The products were purified by recrystallization (Table 3).

exo*-5-(*N*′-Arylureidomethyl)-*endo*-5-methylbicyclo[2.2.1]hept-2-enes XI and XII and *exo*-5-(*N*′-benzylthioureidomethyl)-*endo*-5-methylbicyclo-[2.2.1]hept-2-ene (XIII) (general procedure***).** A solution of 0.14 g (0.01 mol) of amine **II** in 5 ml of benzene was added to a solution of 0.01 mol of appropriate aryl isocyanate or benzyl isothiocyanate in 5 ml of the same solvent. When the reaction was complete (TLC), the precipitate was filtered off, washed with benzene on a filter, dried, and recrystallized from benzene (Table 3).

***exo*-2,3-Epoxy-*endo*-5-methyl-*exo*-5-(*N*′-*p*-tolylsulfonylureidomethyl)bicyclo[2.2.1]heptane (XIV).** A solution of 0.2 g (1.31 mmol) of compound **III** in 3 ml of benzene was added to a solution of 0.22 g (1.31 mmol) of *p*-tolylsulfonyl isocyanate in 3 ml

Table 4. ^{1}H NMR spectra of compounds **V**, **VI**, **XV**, and **XVI**

Comp. no.	Chemical shifts δ, ppm, and coupling constants *J*, Hz									
	1-H	2-H, 3-H	4-H	*exo*-6-H	*endo*-6-H	7-H	8-H_A, 8-H_B	CH_3	NH	H_{arom}
V		3.15		2.25, $^2J_{6,6}$ = 13.0, $^3J_{6,1}$ = 3.8	1.30, $^4J_{6,7}$ = 2.3		–	1.45		–
VI	2.78	6.13, 6.00, $^3J_{2,3}$ = 5.7, $^3J_{2,1}$ = 3.2, $^3J_{3,4}$ = 2.9	2.61	1.54, $^2J_{6,6}$ = 11.8, $^3J_{6,1}$ = 3.8	0.87, $^4J_{6,7}$ = 2.2	1.26, 1.43, $^2J_{7,7}$ = 8.8	3.20, 3.06, $^2J_{8,8}$ = 13.8	0.98	7.79	8.27, 8.03
XV	2.74	6.11, 6.02, $^3J_{2,3}$ = 5.6, $^3J_{2,1}$ = 3.01, $^3J_{3,4}$ = 3.01	2.42	1.37, $^2J_{6,6}$ = 11.8, $^3J_{6,1}$ = 3.9	0.75, $^4J_{6,7}$ = 2.5	1.37, 1.56, $^2J_{7,7}$ = 7.9	3.33, 3.27, $^2J_{8,8}$ = 13.0	0.84	7.59, 5.72	7.35, 7.14
XVI	2.74	5.99, 5.94, $^3J_{2,3}$ = 5.6, $^3J_{2,1}$ = 3.3, $^3J_{3,4}$ = 3.7	2.53	~1.20	1.01, $^2J_{6,6}$ = 11.7, $^3J_{6,5}$ = 3.7	1.28, 1.14, $^2J_{7,7}$ = 10.0	3.02, 2.90, $^2J_{8,8}$ = 2.6, $^3J_{8A,5}$ = 5.9, $^3J_{8B,5}$ = 6.3	–	–	8.31, 8.00

of benzene. When the reaction was complete (TLC), the precipitate was filtered off, washed with benzene on a filter, and dried. The product was recrystallized from isopropyl alcohol (Table 3).

REFERENCES

1. Krieger, H., *Arzneim.-Forsch.*, 1968, vol. 18, pp. 129–134, 324–330, 487–493; US Patent no. 3439100, 1969; *Chem. Abstr.*, 1969, vol. 71, p. 38446d.
2. Kuhla, D.E., Sarges, R., and Barth, W., *J. Heterocycl. Chem.*, 1978, vol. 15, no. 4, pp. 565–567; US Patent no. 3879403, 1975; *Ref. Zh., Khim.*, 1976, no. 5O65; US Patent no. 3992388, 1976; *Chem. Abstr.*, 1977, vol. 86, no. 13987o; Austral. Patent no 220063, 1958; *Ref. Zh., Khim.*, 1961, no. 8L347.
3. Kamata, S., Haga, N., Tsuri, T., Uchida, K., Kakushi, H., Arita, H., and Hanasaki, K., *J. Med. Chem.*, 1990, vol. 33, no. 1, pp. 229–239; Hamanaka, N., Seko, T., Miyazaki, T., Naka, M., Furata, K., and Yamamoto, H., *Tetrahedron Lett.*, 1989, vol. 30, no. 18, pp. 2399–2402; Ohtani, M. and Narisada, M., *J. Med. Chem.*, 1990, vol. 33, no. 3, pp. 1027–1031; Murata, M., Ikoma, S., and Achiva, K., *Chem. Pharm. Bull.*, 1990, vol. 38, no. 8, pp. 2329–2331.
4. Markov, V.I., Kas'yan, A.O., and Selyutin, O.B., *Ukr. Khim. Zh.*, 1994, vol. 60, no. 8, pp. 575–581; Kas'yan, L.I., Kas'yan, A.O., Gorb, L.G., and Klebanov, B.M., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 5, pp. 626–634.
5. Kasyan, L.I., Sereda, S.V., Potekhin, K.A., and Kasyan, A.O., *Heteroatom Chem.*, 1997, vol. 8, no. 2, pp. 177–184.
6. Ukrainian Patent no. 10504A, 1996; *Byull. Izobret.*, 1996, no. 4; Ukrainian Patent Appl. no. 98105581, 1998; Kasyan, L.I., Zlenko, H.T., Kasyan, A.O., Krasnovski, O.Yu., and Gaponova, R.G., Abstracts of Papers, *XIVth Int. Symp. on Medicinal Chemistry*, Maastricht, 1996, p. 308; Kasyan, L.I., Zlenko, H.T., Kasyan, A.O., and Tarabara, I.N., Abstracts of Papers, *XVth Int. Symp. on Medicinal Chemistry*, Maastricht, 1998, p. 204.
7. Kas'yan, A.O., Krasnovskaya, O.Yu., Okovityi, S.I., and Kas'yan, L.I., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 3, pp. 311–319.
8. Sauers, R.R., *J. Am. Chem. Soc.*, 1959, vol. 81, no. 18, pp. 4873–4876; Onishchenko, A.S., *Dienovyi sintez* (Diels–Alder Reaction), Moscow: Akad. Nauk SSSR, 1963.
9. Nakanishi, K., *Infrared Absorption Spectroscopy. Practical*, San Francisco: Holden-Day, 1962.
10. Kas'yan, A.O., Krasnovskaya, O.Yu., Zlenko, E.T., Okovityi, S.I., and Kas'yan, L.I., *Russ. J. Org. Chem.*, 1996, vol. 32, no. 8, pp. 1113–1121.
11. *Molecular Mechanics*, Burkert, U. and Allinger, N.L., Eds., Washington, DC: ACS, 1982.
12. Arbuzov, B.A., Grozina, L.A., Vereshchagin, A.N., and Khamatulina, V.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, no. 4, pp. 787–801.