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New Tricyclic Amides. Synthesis, Structure, and Oxidation with Peroxyphthalic Acid

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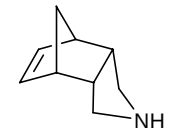
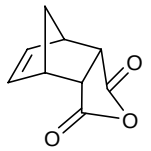
Abstract—4-Azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene was synthesized and brought into reactions with benzoyl, *o*-chlorobenzoyl, *p*-bromobenzoyl, *p*-, *m*-, and *o*-nitrobenzoyl, and bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximidoacetyl chlorides in chloroform in the presence of pyridine. The tricyclic amides thus obtained were epoxidated with peroxyphthalic acid prepared *in situ* by reaction of phthalic anhydride with a 35% aqueous solution of hydrogen peroxide. The structure of newly synthesized compounds was confirmed by IR and ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Their NMR spectra were compared with those of previously synthesized *N*-arylsulfonyl-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-enes on the basis of conformational composition of the corresponding *p*-nitrophenyl-substituted derivatives, which was determined by PM3 semiempirical quantum-chemical calculations.

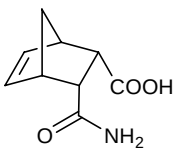
4-Azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**I**) is a product of transformation of accessible stereochemically homogeneous bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboxylic anhydride (endic anhydride, **IIa**). Chemical behavior of compound **I** was studied in a series of publications; its alkylated derivatives and quaternary ammonium salts were studied most thoroughly due to their appreciable biological activity [1]. We previously described reactions of amine **I** with arene-, phenylmethane-, cyclohexane-, and propanesulfonyl chlorides, which resulted in formation of a wide series of sulfonamides; epoxidation of these sulfonamides and their reactions with *p*-nitrophenyl azide at the strained double bond were performed [2]. Amine **I** was brought into reactions with aryl and arylsulfonyl isocyanates and isothiocyanates, benzoyl isocyanate, benzoyl isothiocyanate [3], and endic anhydride [4]. Some sulfonylureas thus obtained exhibited antidiabetic properties [3, 5]. Derivatives of amine **I** were active against Gram-positive and Gram-negative bacteria, and some compounds were found to be morphine antagonists [6, 7]. Among N-(R-carbonyl) derivatives of **I**, only two compounds were reported previously: *N*-chloroacetyl- [8] and *N*-(*p*-toluyl)-4-azatricyclo-[5.2.1.$0^{2,6}$]dec-8-enes [4]. However, their reactivity and possible application were not studied.



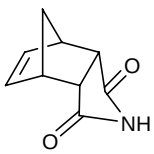
I



IIa



IIb



IIc

The goal of the present work was to synthesize new acyl derivatives of amine **I**, examine their spectral parameters and conformational behavior, and effect their oxidation at the strained double bond with peroxy acids. Initial compound **I** was prepared by the known method [1–4] from accessible endic anhydride (**IIa**) via initial transformation into amido acid **IIb** (NH_4OH, benzene, 20–25°C) and subsequent cyclization to imide **IIc** (heating in boiling acetic acid) and reduction with $LiAlH_4$ in boiling diethyl ether.

Amine **I** reacted with substituted benzoyl chlorides in chloroform in the presence of an equimolar amount of pyridine as base (Scheme 1) to afford carboxamides **IIIa**–**IIIf**. Amide **V** having an additional cage-like fragment was synthesized from bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximidoacetic acid (**IVa**) [9] through the corresponding carbonyl chloride **IVb** (Scheme 2).

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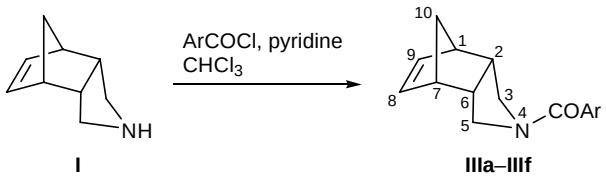
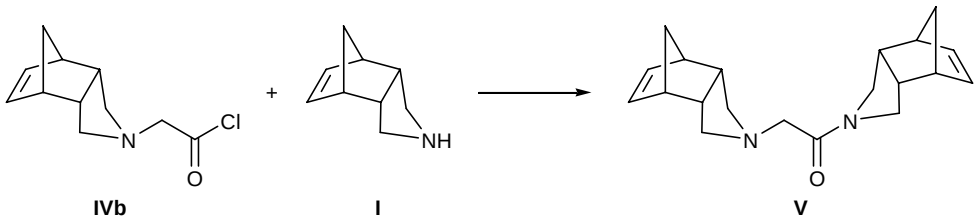
Scheme 1.



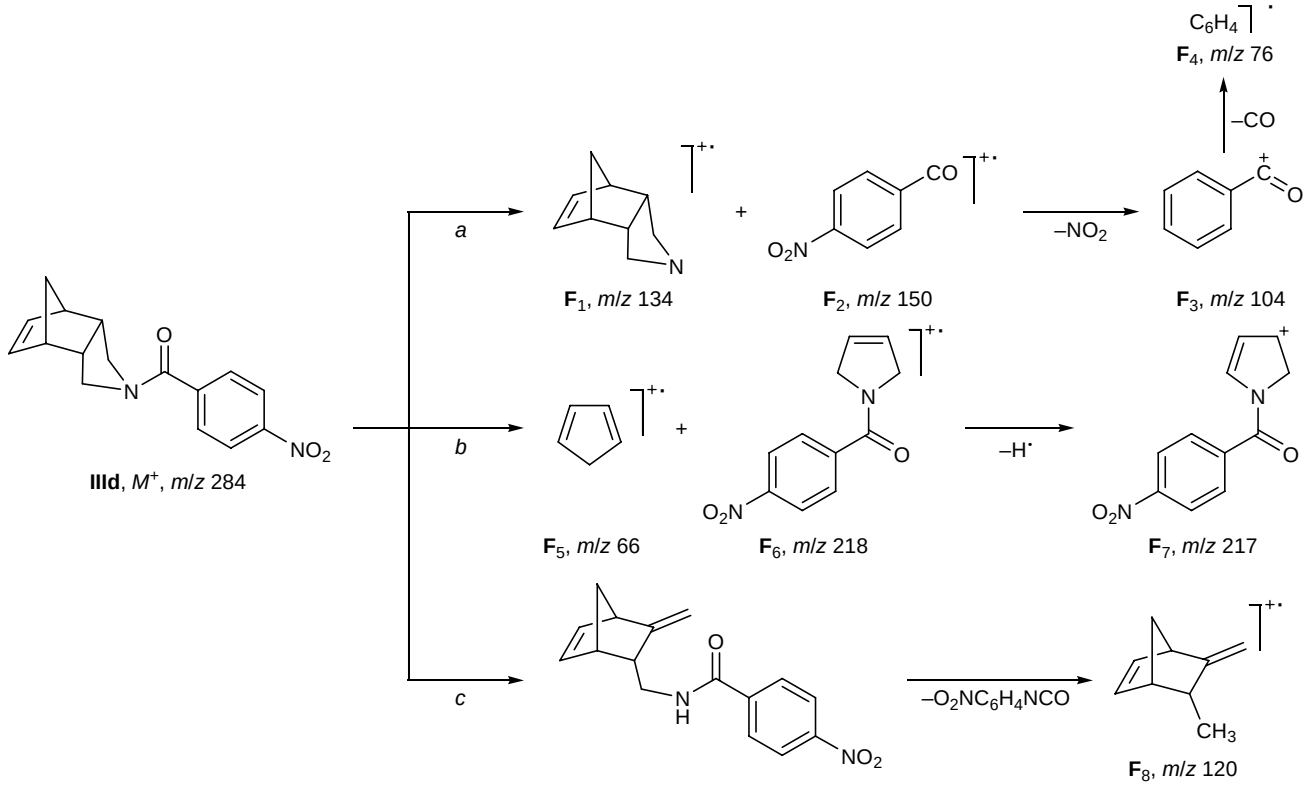
Ar = Ph (**a**), *o*-ClC_6H_4 (**b**), *p*-BrC_6H_4 (**c**), *p*-$O_2NC_6H_4$ (**d**), *m*-$O_2NC_6H_4$ (**e**), *o*-$O_2NC_6H_4$ (**f**).

Scheme 2.



The structure of amides **IIIa**–**IIIf** and **V** was confirmed by spectral methods. Their IR spectra contained absorption bands in the regions 3068–3040 [ν(=C–H)] and 735–700 cm^{-1} [(δ(=C–H)]. The position of the first of these allows us to distinguish between strained double bonds in compounds **III** and **V** and those in terminal alkenes (3080 cm^{-1}) and cyclohexene (3027 cm^{-1}) [10]. In the IR spectra of compounds containing aromatic fragments, this band is obscured by absorption of aromatic C–H bonds; however, amide **V** showed a distinct absorption band at 3040 cm^{-1}. The IR spectrum of **V** also contained a weak band at 1560 cm^{-1}, which belongs to stretching vibrations of the strained C=C bond [11]. The corresponding band in the spectra of aromatic amides is usually overlapped by absorption due to stretching vibrations of aromatic

Scheme 3.

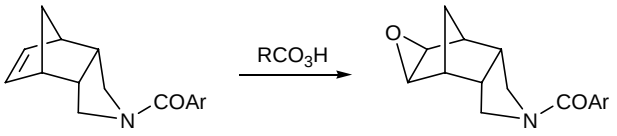


C–C bonds. The IR spectra of amides **III** and **V** lacked N–H absorption, but two amide bands at 1640–1625 (νC=O) and 1250–1180 cm^{-1} (νC–N) [10] were present.

Scheme 3 shows the fragmentation pattern of amide **IIId** under electron impact. Three main fragmentation pathways can be distinguished. Pathway *a* includes decomposition of the molecular ion via cleavage of the C–N bond with formation of radical ions $\mathbf{F}_1$ and $\mathbf{F}_2$ and subsequent fragmentation of $\mathbf{F}_2$ to ions $\mathbf{F}_3$ and $\mathbf{F}_4$. According to pathway *b*, retro-Diels–Alder decomposition of the molecular ion gives radical ions $\mathbf{F}_5$ and $\mathbf{F}_6$, and the latter is then converted into ion $\mathbf{F}_7$. Pathway *c* involves cleavage of one C–N bond in the tetrahydropyrrole ring, followed by elimination of neutral *p*-nitrophenyl isocyanate molecule with formation of radical ion $\mathbf{F}_8$. The observed fragmentation pattern indicates predominant contribution of pathway *a* (the intensity of signals with *m*/*z* 150 is about ~100%) [12].

Amides **IIIb** and **IIId** were subjected to epoxidation by treatment with peroxyphthalic acid generated *in situ* from phthalic anhydride and 35% aqueous hydrogen peroxide in ethyl acetate in the presence of urea; the latter was added to control proton-donor and proton-acceptor properties of the medium [13]. Epoxy derivatives **VIa** and **VIb** were isolated in 70–80% yield (Scheme 4).

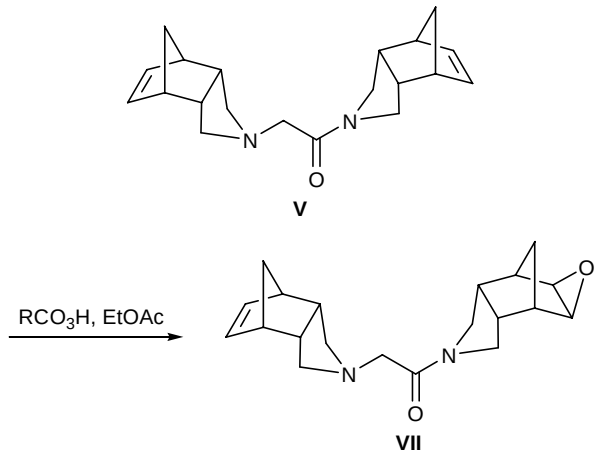
Scheme 4.



IIIb, **IIId** **VIb**, **VIb**

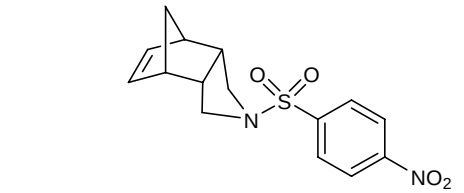
Epoxidation of amide **V** attracts a specific interest, for the substrate possesses two double bonds in cage-like fragments with different substituents. The optimal epoxidating agent for olefins with a hydrogenated isoindole fragment is peroxyphthalic acid, while more reactive peroxyformic acid seems to be the most appropriate for epoxidation of the fragment containing electron-acceptor carbonyl groups; peroxyformic acid was successfully used in the epoxidation of carboximides of the norbornene series [14]. However, taking into account that oxidation with peroxyformic acid is sometimes accompanied by side molecular rearrangements and hydroxylation processes [15], we used peroxyphthalic acid (prepared *in situ*) in an amount corresponding to epoxidation of both double bond. As a result, we isolated monoepoxy derivative **VII** in 83.9% yield (Scheme 5). In the IR spectra of compounds **VIa**, **VIb**, and **VII** we observed a strong absorption band at 855–850 cm^{-1} due to stretching vibrations of the C–O bond in the epoxynorbornane fragment [16].

Scheme 5.

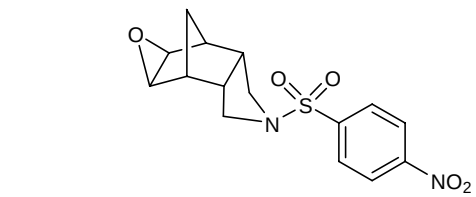


V **VII**

Analysis of the ^{1}H NMR spectra of amides **IIIa**–**IIIf** revealed considerable differences from the spectrum of previously described sulfonamide **VIII** [2]. The 8-H/9-H, 1-H/7-H, and 2-H/6-H protons in **IIIa**–**IIIf** were nonequivalent in pairs, and in some cases the difference in the chemical shifts exceeded 0.2–0.3 ppm. As in the spectra of sulfonamides, appreciable differences in chemical shifts were observed for 3-H_A/3-H_B and 5-H_A/5-H_B, i.e., protons located at different sides of the amide fragment; the geminal coupling constants for the above protons range from 11.5 to 13.5 Hz. Analogous differences were also observed between epoxy derivatives **VIa** and **VIb**, on the one hand, and sulfonamide **IX**, on the other. Amides **VIa** and **VIb** are characterized by a downfield shift of



VIII



IX

signals from protons on C^3 and C^5, especially of the 3-H_A signal (from δ 3.59 to 4.35 ppm). Some specific features were also revealed by analysis of the ^{13}C NMR spectra of compounds **IIId** and **VIII**. The difference in the chemical shifts of C^2 and C^6 in the spectrum of amide **IIId** reached 2.0 ppm.

Amide **V** displayed in the ^1H NMR spectrum signals from both norbornene fragments (amine and acid components). The symmetric bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximide fragment gave signals at δ 6.06, 3.31, and 2.85 ppm; protons in the bridging methylene group appeared as doublets at δ 1.66 and 1.38 ppm with a coupling constant of 8.7 Hz. Signals from protons in the other methylene bridge (amine component) were located at δ 1.51 and 1.49 ppm (^3J = 8.0 Hz), as in the spectra of arenecarboxamides **IIIa**–**IIIf**. The ^1H NMR spectrum of **V** also contained a two-proton signal at δ 3.83 ppm belonging to the methylene group connecting the imide and carbonyl moieties. The corresponding carbon signal was located at δ_C 40.1 ppm in the ^{13}C NMR spectrum. The signal from the amide carbonyl carbon atom appeared at δ_C 162.7 ppm, and equivalent carbonyl carbon atoms of the imide fragment gave a signal at δ_C 177.3 ppm.

Protons at the oxirane ring in compounds **VIa**, **VIb**, and **VII** resonated at δ 3.21–3.43 ppm. Characteristically, the *anti*-10-H signal was displaced upfield (δ 0.78–0.86 ppm) due to magnetically anisotropic effect of the three-membered ring [17]. These data are consistent with the differences between the ^1H NMR spectra of epoxy derivative **IX** and its unsaturated analog **VIII**. In the ^{13}C NMR spectra of **VIa** and **IX**, signals from carbon atoms in the oxirane ring were located at δ_C 48–50 ppm, and the C^{10} signal was displaced upfield. The chemical shifts of C^{10} in **IIId** and **VIa** are 48.6 and 29.4 ppm, respectively (cf. δ_C 52.6 and 29.6 ppm for sulfonamides **VIII** and **IX**, respectively) [18].

The ^1H NMR spectrum of **VII** contained signals from protons in both olefinic (δ 6.01 ppm) and epoxy fragments (δ 3.39 ppm). The position of signals from protons in the methylene bridge (δ 1.20 and 0.78 ppm, $^2J_{syn\text{-}10,anti\text{-}10}$ = 9.2 Hz) indicates that the oxirane ring is located in the amine fragment; protons of the bridging methylene group in the imide fragment give signals at about δ 1.54 ppm, in keeping with published data [14]. As in the spectrum of unsaturated precursor **V**, couples of protons in the amine fragment of **VII** (1-H/7-H, 2-H/6-H) have different chemical shifts; the same applies to protons attached to C^3 and C^5 (δ 3.38, 3.30, 3.24, and 3.05 ppm). By contrast, the corresponding protons in the imide fragment are equivalent, δ, ppm: 3.31 (1-H/7-H), 3.07 (2-H/6-H). These data indicate selective epoxidation with peroxyphthalic acid of the more nucleophilic olefinic fragment in molecule **V**.

Considerable differences in the NMR spectra of carboxamides and sulfonamides derived from 4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene should reflect their specific conformational properties. Using the PM3 semiempirical quantum-chemical method [19], we analyzed the conformational composition of structurally related *p*-nitrobenzoylamide **IIId** and *p*-nitrobenzenesulfonamide **VIII**. The calculations were performed with account taken of possible differences in the conformations of the five-membered nitrogen-containing ring

Principal torsion angles (deg) and energy parameters of stable conformers of compounds **IIId** and **VIII**, calculated by the PM3 method

Comp. no.	Conformer	$C^2C^3N^4C^5$	$CS(C)N^4C^5$	$CS(C)N^4C^3$	$O^1S(C)N^4C^5$	$O^1S(C)N^4C^6$	$C^2C^3N^4H^R$	H_f, a.u.	$H_{f\,rel}$, a.u.
IIId	**A**	5.9	–167.9	–24.4	16.8	160.3	–140.6	10.92	0.49
	B	6.0	24.3	167.9	–160.4	–16.9	–140.5	10.92	0.49
	C	–4.2	–23.0	–164.4	161.6	20.2	140.4	10.43	0
	D	6.7	–14.2	–156.8	–156.8	–14.2	152.0	11.07	0.64
VIII	**E**	11.3	–106.4	109.0	7.9	–5.4	159.2	–13.76	0
	F	11.2	–109.3	106.1	4.9	–8.3	158.9	–13.76	0
	G	13.3	78.5	–73.8	35.8	41.1	168.3	–13.08	0.68
	H	14.1	89.8	–127.0	–24.5	–12.6	–132.8	–13.43	0.33
	I	12.8	112.6	–102.6	24.5	11.7	–135.0	–13.43	0.33
	J	9.5	–74.7	74.5	39.7	–39.9	–142.8	–12.89	0.88

(*syn*- and *anti-envelopes*) and orientations of the substituent on the nitrogen atom (*endo* and *exo*). Specific features in the stereochemical structure of molecules **IIId** and **VIII** were characterized by the dihedral angles $C^2C^3N^4C^5$ and $C^2C^3N^4N$ (see table), by the possibility for rotation of the amide (or sulfonamide) moiety about the N–C(S) bond, and by spatial orientation of the substituent.

Calculations of amide **IIId** showed that, among four possible conformers **A**–**D** (Fig. 1), structures **A** and **B** are mirror isomers. Structures **C** and **D** differ by conformation of the five-membered fragment and thermodynamic stability. Conformer **C** is the most stable, while structure **D** is the least stable. No symmetric conformers were found, and the contributions of conformers **C** and **D** differed in keeping with their thermodynamic stabilities (see table). These data suggest nonequivalence of twin ^1H and ^{13}C nuclei in the tricyclic skeleton, as was really observed in the ^1H and ^{13}C NMR spectra of compound **IIId**.

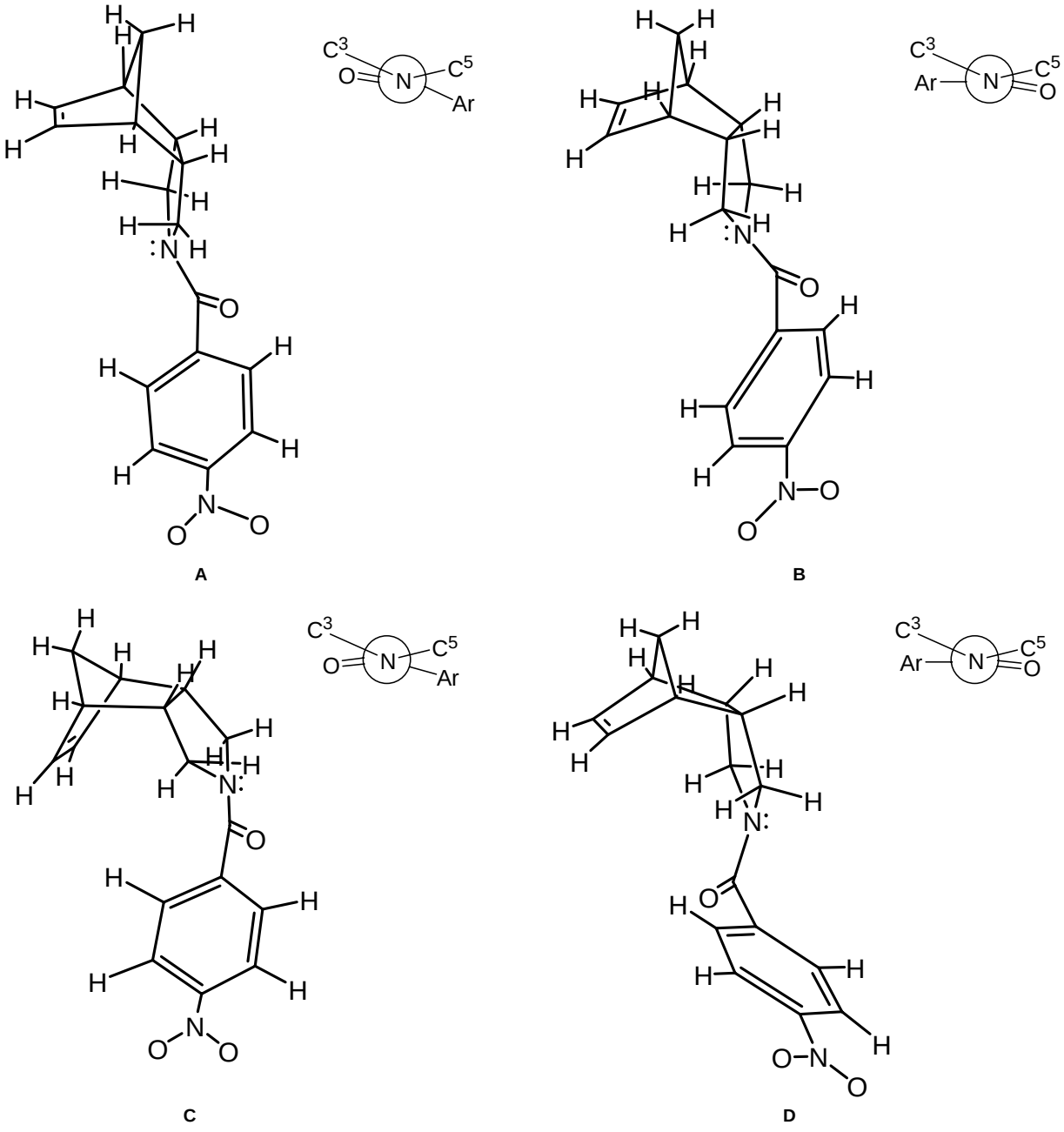


Fig. 1. Possible conformers of *N*-(*p*-nitrobenzoyl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**IIId**) according to the PM3 calculations.

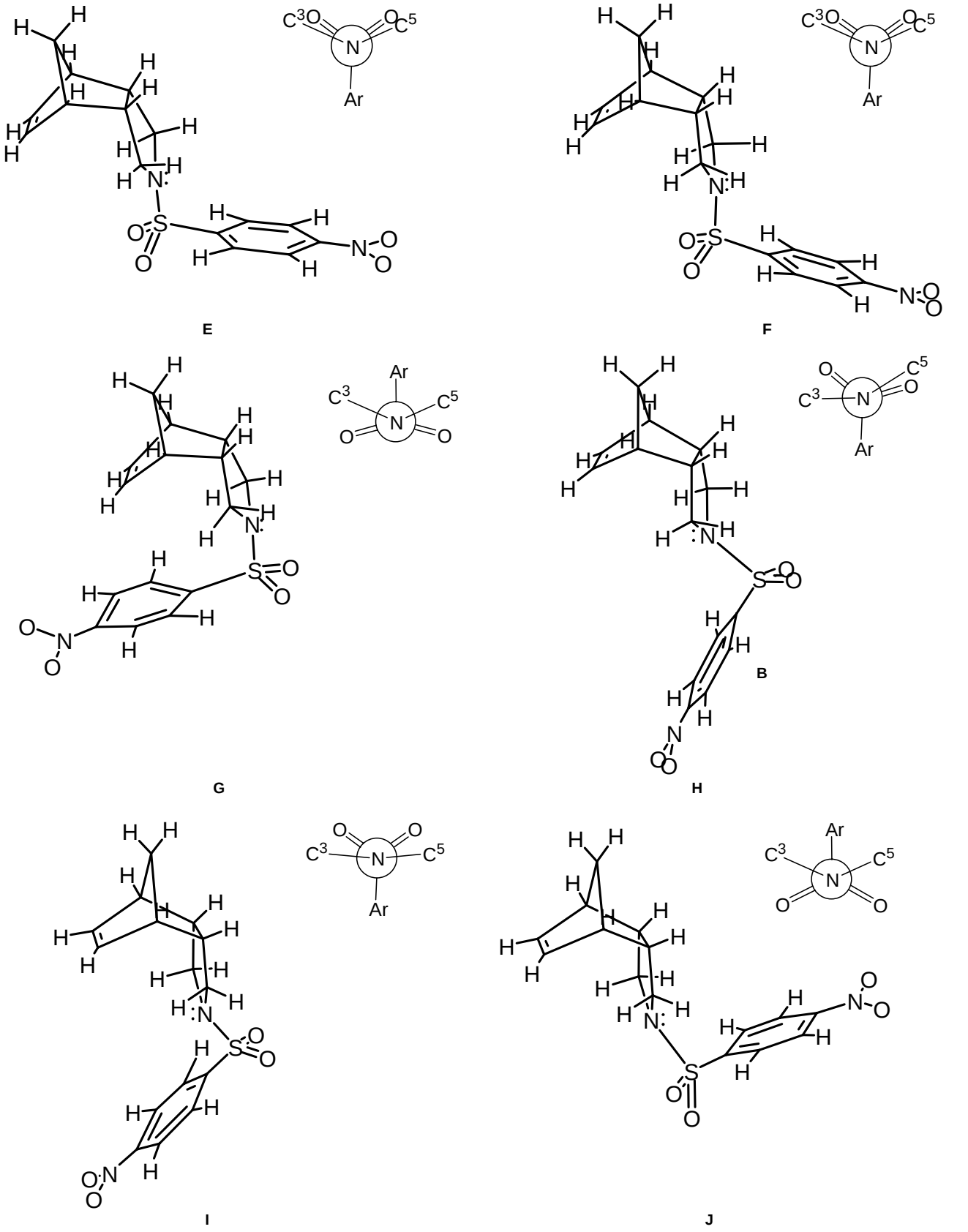


Fig. 2. Possible conformers of *N*-(*p*-nitrophenylsulfonyl)-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (**VIII**) according to the PM3 calculations.

Analysis of the steric structure of sulfonamide **VIII** revealed six conformers with *anti* configuration of the isoindole envelope (Fig. 2). Three of these (**E**–**G**) are characterized by *endo* orientation of the sulfonamide fragment, and the other three (**H**–**J**) have *exo*-oriented N–S bond. The orientation of substituents with respect to the N–SO_2 bond in conformers **E**, **F**, and **J** is transoid, while it is cisoid in structures **G**, **H**, and **I**. The thermodynamic stability of sulfonamide **VIII** conformers decreases in the series **E** = **F** > **H** = **I** > **G** > **J**.

Taking into account that conformers **E**/**F** and **H**/**I** have similar heats of formation (mirror isomers) and that structures **G** and **J** are almost symmetric (the symmetry plane passes through the C^{10}, N, and S atoms), equal electronic and magnetic shielding of protons (8-H/9-H, 1-H/7-H, 2-H/6-H) and carbon nuclei (C^8/C^9, C^1/C^7, C^2/C^6, C^3/C^5) in the rigid skeleton might be expected. Thus conformational analysis of compounds **IIId** and **VIII** allowed us to interpret differences in the ^{1}H and ^{13}C NMR spectra of carboxamides and sulfonamides derived from tricyclic amine **I**.

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on Bruker DRX-500 (500 MHz) and Inova-400 (400 MHz) spectrometers from solutions in DMSO-d_6 or $CDCl_3$ using tetramethylsilane as internal reference. The ^{13}C NMR spectra were obtained on an Inova-400 instrument at 100.6 MHz. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent; spots were visualized by treatment with iodine vapor. The elemental analyses were obtained using a Carlo Erba analyzer.

4-Azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**I**) was prepared by the procedure described in [4]; its properties were consistent with published data.

Reaction of 4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (I) with acid chlorides (*general procedure*). A solution of 2.2 mmol of the corresponding acid chloride in 5 ml of dry chloroform was added dropwise under stirring at room temperature to a mixture of 0.3 g (2.2 mmol) of compound **I** and 0.18 ml (2.2 mmol) of pyridine in 10 ml of dry chloroform. When the reaction was complete (TLC), the mixture was washed with water, 20% hydrochloric acid, and water again. The organic phase was separated, dried over calcined magnesium sulfate, and evaporated, and the residue was subjected to column chromatography on silica gel using diethyl ether as eluent to isolate compound **IIIa**–**IIIf** or **V**.

***N*-Benzoyl-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (IIIa).** Yield 69.0%, oily substance. IR spectrum, ν, cm^{-1}: 3065, 1705, 1620, 1592, 1450, 1288, 712. ^{1}H NMR spectrum, δ, ppm: 7.34–7.96 m (4H, H_{arom}), 6.22 m (1H, 8-H), 5.96 m (1H, 9-H), 3.52 m (1H, 3-H_A), 3.37 m (1H, 3-H_B), 3.25 m (1H, 5-H_A), 2.95 m (1H, 1-H), 2.95 m (1H, 2-H), 2.85 m (1H, 5-H_B), 2.77 m (1H, 7-H), 2.74 m (1H, 6-H), 1.47 d (1H, *syn*-10-H), 1.38 d (1H, *anti*-10-H). Found, %: N 5.70. $C_{16}H_{17}NO$. Calculated, %: N 5.86.

***N*-(*o*-Chlorobenzoyl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (IIIb).** Yield 85.4%, mp 76–77°C. IR spectrum, ν, cm^{-1}: 3072, 1645, 1604, 1478, 1440, 1242, 1062, 725. ^{1}H NMR spectrum, δ, ppm: 7.14–7.33 m (4H, H_{arom}), 6.26 m (1H, 8-H), 6.09 m (1H, 9-H), 3.38 m (1H, 3-H_A), 3.33 m (1H, 3-H_B), 3.24 m (1H, 5-H_A), 2.94 m (1H, 1-H), 2.85 m (1H, 5-H_B), 2.84 m (1H, 2-H), 2.78 m (1H, 7-H), 2.70 m (1H, 6-H), 1.52 d (1H, *syn*-10-H), 1.39 d (1H, *anti*-10-H). Found, %: N 5.32. $C_{16}H_{16}ClNO$. Calculated, %: N 5.12.

***N*-(*p*-Bromobenzoyl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (IIIc).** Yield 82.1%, mp 135–136°C. ^{1}H NMR spectrum, δ, ppm: 7.50 d (2H, H_{arom}), 7.24 d (2H, H_{arom}), 6.20 m (1H, 8-H), 5.96 m (1H, 9-H), 3.52 m (1H, 3-H_A), 3.38 m (1H, 3-H_B), 3.23 m (1H, 5-H_A), 2.97 m (1H, 2-H), 2.95 m (1H, 1-H), 2.95 m (1H, 5-H_B), 2.80 m (1H, 6-H), 2.78 m (1H, 7-H), 1.47 d (1H, *syn*-10-H), 1.37 d (1H, *anti*-10-H). Found, %: N 4.47. $C_{16}H_{16}BrNO$. Calculated, %: N 4.40.

***N*-(*p*-Nitrobenzoyl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (IIId).** Yield 78.6%, mp 101–102°C. IR spectrum, ν, cm^{-1}: 3114, 3043, 1627, 1598, 1521, 1430, 1352, 709. ^{1}H NMR spectrum, δ, ppm: 8.19 d (2H, H_{arom}), 7.47 d (2H, H_{arom}), 6.24 d.d (1H, 8-H, $^3J_{8,9}$ = 5.6, $^3J_{8,7}$ = 3.0 Hz), 5.96 d.d (1H, 9-H, $^3J_{9,1}$ = 2.8 Hz), 3.59 d.d (1H, 3-H_A, $^2J_{3A,3B}$ = 13.5, $^3J_{3A,2}$ = 2.8 Hz), 3.33 d.d (1H, 3-H_B, $^3J_{3B,2}$ = 2.8 Hz), 3.32 d (1H, 5-H_A, $^2J_{5A,5B}$ = 11.5 Hz), 2.92 m (1H, 2-H), 2.88 m (1H, 1-H), 2.85 m (1H, 7-H), 2.83 d (1H, 5-H_B), 2.77 m (1H, 6-H), 1.47 d (1H, *syn*-10-H, $^2J_{syn\text{-}10,anti\text{-}10}$ = 8.4 Hz), 1.34 d (1H, *anti*-10-H). ^{13}C NMR spectrum, δ, ppm: 166.7 (C=O), 148.1 (C_{arom}), 143.8 (C_{arom}), 135.9 (C^9), 134.8 (C^8), 52.1 (C^5), 51.9 (C^3), 48.1 (C^{10}), 47.0 (C^1, C^7), 46.1 (C^6), 44.0 (C^2). Found, %: N 9.98. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.86.

***N*-(*m*-Nitrobenzoyl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (IIIe).** Yield 72.4%, oily substance. ^{1}H NMR spectrum, δ, ppm: 7.66–8.24 m (4H, H_{arom}), 6.25 m (1H, 8-H), 6.00 m (1H, 9-H), 3.53 m (1H, 3-H_A), 3.48 m (1H, 3-H_B), 3.32 m (1H, 5-H_A), 2.97 m (1H, 2-H), 2.95 m (1H, 5-H_B), 2.90 m (1H, 6-H), 2.89 m

(1H, 1-H), 2.82 m (1H, 7-H), 1.47 d (1H, *syn*-10-H), 1.41 d (1H, *anti*-10-H). Found, %: N 9.90. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.86.

***N*-(*o*-Nitrobenzoyl)-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (IIIf).** Yield 71.8%, oily substance. IR spectrum, ν, cm^{-1}: 3068, 1707, 1634, 1531, 1430, 1350, 1258, 715. ^{1}H NMR spectrum, δ, ppm: 7.29–8.08 m (4H, H_{arom}), 6.32 m (1H, 8-H), 6.14 m (1H, 9-H), 3.37 m (1H, 3-H_A), 3.30 m (1H, 3-H_B), 3.23 m (1H, 5-H_A), 2.96 m (1H, 5-H_B), 2.85 m (1H, 1-H), 2.80 m (1H, 7-H), 2.75 m (1H, 2-H), 2.67 m (1H, 6-H), 1.52 d (1H, *syn*-10-H), 1.43 d (1H, *anti*-10-H). Found, %: N 9.77. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.86.

Bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximidoacetyl chloride (IVb) was synthesized according to the procedure described in [9, 12].

***N*-(Bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximidoacetyl)-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (V)** was synthesized by the procedure described above for compounds **IIIa**–**IIIf** from chloride **IVb** and amine **I**. Yield 93.0%, mp 188–189°C. IR spectrum, ν, cm^{-1}: 3040, 2985, 2910, 1780, 1725, 1675, 1560, 1460, 1195, 750. ^{1}H NMR spectrum, δ, ppm: 6.14 m (2H, 8-H, 9-H), 6.06 m (2H, 8'-H, 9'-H), 3.83 m (2H, CH_2), 3.36 m (1H, 6-H), 3.31 m (2H, 1'-H, 7'-H), 3.29 m (1H, 3-H_A), 3.29 m (1H, 1-H), 3.25 m (1H, 5-H_A), 3.11 m (1H, 5-H_B), 2.97 m (1H, 7-H), 2.94 m (1H, 2-H), 2.85 m (2H, 2'-H, 6'-H), 2.81 m (1H, 3-H_B), 1.66 d (1H, *syn*-10'-H, $^2J_{syn\text{-}10',anti\text{-}10'}$ = 8.7 Hz), 1.51 d (1H, *syn*-10-H, $^2J_{syn\text{-}10,anti\text{-}10}$ = 8.0 Hz), 1.49 m (1H, *anti*-10-H), 1.38 m (1H, *anti*-10'-H). ^{13}C NMR spectrum, δ_C, ppm: 177.3 (C=O), 177.3 (C=O), 162.7 (C=O), 136.5 (C^9), 135.0 (C^8), 134.8 ($C^{8'}$, $C^{9'}$), 52.5 (C^5), 52.2 (C^3), 48.6 (C^{10}), 48.5 ($C^{10'}$), 46.8 (C^1, C^7), 46.5 ($C^{1'}$), 46.4 (C^6), 46.4 ($C^{7'}$), 45.2 (C^2), 45.0 ($C^{2'}$), 44.0 ($C^{6'}$). Found, %: N 8.19. $C_{20}H_{22}N_2O_3$. Calculated, %: N 8.28.

Oxidation of compounds IIIb, IIId, and V with peroxyphthalic acid (*general procedure*). To a mixture of 0.6 mmol of carboxamide **IIIb**, **IIId**, or **V**, 0.18 g (1.2 mmol) of phthalic anhydride, and 0.02 g (0.3 mmol) of urea in 15 ml of ethyl acetate we added under stirring at room temperature 0.11 g (0.1 ml, 2 mmol) of a 35% aqueous solution of hydrogen peroxide. The mixture was stirred until the reaction was complete (TLC) and neutralized with a saturated solution of sodium carbonate, the organic phase was separated, dried over calcined magnesium sulfate, and evaporated, and the product (compound **VIa**, **VIb**, or **VII**) was recrystallized from appropriate solvent.

***N*-(*p*-Nitrobenzoyl)-*exo*-8,9-epoxy-4-azatricyclo-[5.2.1.0^{2,6}]decane (VIa)** was obtained from amide **IIId**. Yield 76.3%, mp 187–189°C. IR spectrum, ν, cm^{-1}: 3050, 1626, 1598, 1517, 1351, 1295, 1204, 850. ^{1}H NMR spectrum, δ, ppm: 7.63 d (2H, H_{arom}), 7.60 d (2H, H_{arom}), 4.35 m (1H, 3-H_A, $^2J_{3A,3B}$ = 13.5 Hz), 3.47 m (1H, 5-H_A, $^2J_{5A,5B}$ = 12.1 Hz), 3.43 m (1H, 8-H), 3.39 m (1H, 9-H), 3.30 m (1H, 3-H_B), 2.94 m (1H, 5-H_B), 2.88 m (1H, 1-H), 2.77 m (1H, 7-H), 2.69 m (1H, 2-H), 2.54 m (1H, 6-H), 1.46 d (1H, *syn*-10-H, $^2J_{syn\text{-}10,anti\text{-}10}$ = 10.4 Hz), 0.86 d (1H, *anti*-10-H). ^{13}C NMR spectrum, δ_C, ppm: 166.4 (C=O), 148.8 (C_{arom}), 142.8 (C_{arom}), 128.2 (C_{arom}), 123.9 (C_{arom}), 50.0 (C^5), 49.9 (C^9), 48.3 (C^8), 45.2 (C^3), 44.9 (C^7), 44.0 (C^1), 43.0 (C^6), 40.9 (C^2), 24.9 (C^{10}). Found, %: N 9.22. $C_{16}H_{16}N_2O_4$. Calculated, %: N 9.33.

***N*-(*o*-Chlorobenzoyl)-*exo*-8,9-epoxy-4-azatricyclo[5.2.1.0^{2,6}]decane (VIb)** was obtained from amide **IIIb**. Yield 75.2%, mp 95–96°C. IR spectrum, ν, cm^{-1}: 3080, 3050, 3020, 1625, 1568, 1240, 1215, 853. ^{1}H NMR spectrum, δ, ppm: 7.40–7.20 m (4H, H_{arom}), 4.16 m (1H, 3-H_A), 3.37 m (1H, 8-H), 3.35 m (1H, 9-H), 3.33 m (1H, 3-H_B), 3.23 m (1H, 5-H_A), 3.13 m (1H, 5-H_B), 2.73 m (2H, 1-H, 7-H), 2.65 m (1H, 2-H), 2.49 m (1H, 6-H), 1.43 d (1H, *syn*-10-H), 0.83 d (1H, *anti*-10-H). Found, %: N 4.99. $C_{16}H_{16}ClNO_2$. Calculated, %: N 4.84.

***N*-(Bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximidoacetyl)-*exo*-8,9-epoxy-4-azatricyclo-[5.2.1.0^{2,6}]decane (VII)** was obtained from compound **V**. Yield 83.9%, mp 218–220°C. IR spectrum, ν, cm^{-1}: 1780, 1720, 1675, 1455, 1350, 1195, 860. ^{1}H NMR spectrum, δ, ppm: 6.01 m (2H, 8'-H, 9'-H), 4.13 m (1H, CH_2), 3.85 m (1H, CH_2), 3.39 m (2H, 8-H, 9-H), 3.38 m (1H, 3-H_A), 3.31 m (2H, 1'-H, 7'-H), 3.30 m (1H, 3-H_B), 3.28 m (1H, 1-H), 3.24 m (1H, 5-H_A), 3.07 m (2H, 2'-H, 6'-H), 3.05 m (1H, 5-H_B), 3.01 m (1H, 7-H), 2.96 m (1H, 2-H), 2.84 m (1H, 6-H), 1.54 d (2H, *syn*-10'-H, *anti*-10'-H, $^2J_{syn\text{-}10',anti\text{-}10'}$ = 8.5 Hz), 1.20 d (1H, *syn*-10-H, $^2J_{syn\text{-}10,anti\text{-}10}$ = 9.2 Hz), 0.78 d (1H, *anti*-10-H). Found, %: N 7.98. $C_{20}H_{22}N_2O_4$. Calculated, %: N 7.91.

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