Russian Journal of Organic Chemistry, Vol. 41, No. 10, 2005, pp. 1530–1538. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 10, 2005, pp. 1561–1570.

Dedicated to Full Member of the Russian Academy of Sciences N.S. Zefirov on His 70th Anniversary

Acylation of Aminopyridines and Related Compounds with Endic Anhydride

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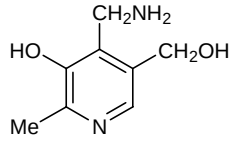
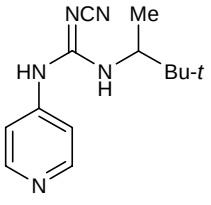
Received May 23, 2005

Abstract—Reactions of bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxanhydride (endic anhydride) with 2-, 3-, and 4-aminopyridines, 3-hydroxy- and 5-iodo-2-aminopyridines, 6-aminoquinoline, and 6-aminoquinoxaline involve chemoselective transformation of the exocyclic amino group. The resulting amido acids were converted into the corresponding carboximides, and the latter were epoxidated with peroxy acids. The structure of the products was confirmed by the IR, UV, and ^{1}H and ^{13}C NMR spectra, as well as by calculation of the ^{1}H and ^{13}C chemical shifts using the GIAO method (B3LYP/6-31G** approximation).

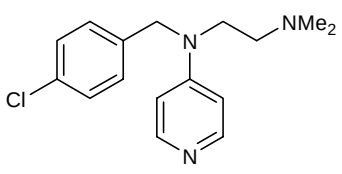
Aromatic pyridine ring plays an important role in metabolism of living organisms [1]. Pyridine derivative pyridoxine (vitamin B_6) participates in one of the main amino acid exchange processes, transamination [2, 3], and pyridoxamine (**Ia**) is an intermediate product in the synthesis of pyridoxine [4]. Pyridine ring constitutes a structural fragment of alkaloids nicotine and anabasine. 4-Aminopyridine affects peripheral neuromediator processes and is used in medical practice for the treatment of residual muscle paralysis.



Ia

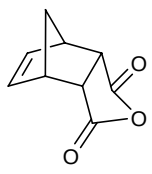


Ib



Ic

· HCl



II

Pinacidil (**Ib**) is a 4-aminopyridine derivative which is known to activate potassium channels. Medical agents on the basis of 2-aminopyridine are more widely known; among these, antimicrobial agents Sulfidine and Sulfasalazine, hypnotic agent Imovane, and Suprastin (**Ic**) possessing antihistaminic and peripheral anticholinergic activity [4].

The present article reports on the reactions of bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic (endic) anhydride (**II**) with aminopyridines **IIIa**–**IIIe** and structurally related 6-aminoquinoline (**IIIf**) and 6-aminoquinoxaline (**IIIg**), subsequent transformation of the adducts thus formed into the corresponding carboximides, and epoxidation of the latter with peroxyformic acid. The reactions were carried out under mild conditions (in benzene at room temperature) to avoid dehydration of amido acids **IVa**–**IVg** to give carboximides **Va**–**Vg** [5] (Scheme 1). The structure of amines **IIIa**–**IIIg** implies the possibility for their unusual acylation and oxidation of imides **Va**–**Vd** which contain additional nitrogen and oxygen nucleophilic centers together with the double bond.

In fact, both 2- and 4-aminopyridines can exist as two tautomers, the amino form being more stable.

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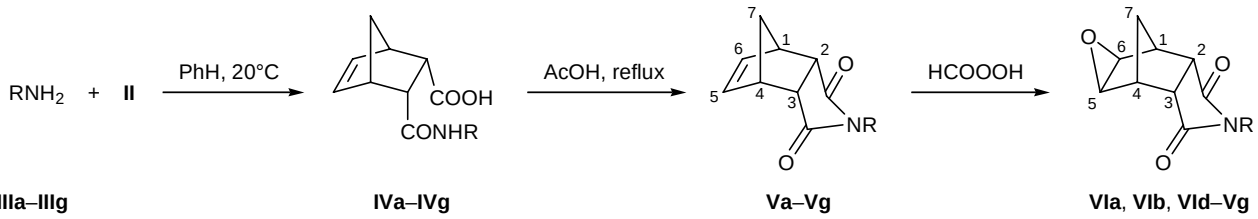
Scheme 1.



IIIa–IIIg **IVa–IVg** **Va–Vg** **VIa**, **VIb**, **VId–Vg**

R = 2-pyridyl (**a**), 3-pyridyl (**b**), 4-pyridyl (**c**), 3-hydroxy-2-pyridyl (**d**), 5-iodo-2-pyridyl (**e**), 6-quinolyl (**f**), 6-quinoxalyl (**g**).

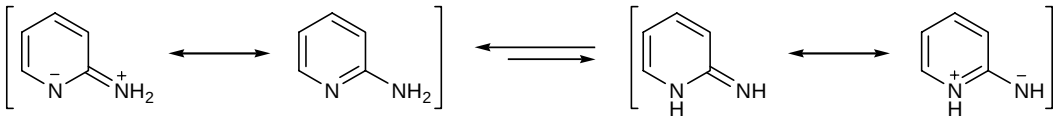
According to Goldfarb *et al*. [6], there is no need of considering the iminopyridine structure **A** as intermediate in the formation of substituted iminopyridines in the alkylation of aminopyridines (Scheme 2). Unlike alkylation reactions whose regioselectivity depends on pH [3], acetylation occurs mainly at the exocyclic amino group [1, 7]; aminopyridines **IIIa** and **IIIb** react with succinic anhydride just in that way [8]. The regioselectivity in the reactions of amines **IIIa**–**IIIg** with endic anhydride was studied by spectral methods. The IR and ^{1}H NMR spectra of the aminolysis products did not contradict the assumed structure of amido acids **IVa**–**IVg**. In the IR spectra of these compounds we observed absorption bands at 1585–1570 (δ_{N-H}, amide II) and 1265–1255 cm^{-1} (ν_{C-N}, amide III) [9]. Each compound **IVa**–**IVg** showed in the spectrum a distinct absorption band at 3370–3250 cm^{-1} due to N–H stretching vibrations and carbonyl absorption band of the carboxy group at 1720–1710 cm^{-1}. The amide carbonyl stretching vibration band was overlapped by absorption of C=N bonds in the heterocyclic fragment (1655–1635 cm^{-1}) [9]. Absorption bands belonging to the unsaturated norbornene fragment were generally obscured by absorption of aromatic C=C bonds. A characteristic band is observed at 725–710 cm^{-1}; it originates from bending vibrations of the =C–H bond at the strained double C=C bond [10].

The ^{1}H NMR spectra of compounds **IVa**, **IVb**, **IVe**, and **IVg** contained multiplets from the nonequivalent 5-H and 6-H protons in the olefinic fragment (δ 6.05–6.20 ppm). Signals from the bridgehead 1-H and 4-H protons and *exo*-2-H and *exo*-3-H were located in a stronger field. These signals can readily be distinguished: the bridgehead protons give unresolved multiplets, while 2-H and 3-H are coupled with each other through a constant ^3J of 8–10 Hz. The latter value unambiguously indicates *exo* orientation of the 2-H and 3-H protons and hence *endo* orientation of the substituents on C^2 and C^3. Stereoisomeric structures with *exo*,*endo* and *endo*,*endo* orientation of 2-H and 3-H are characterized by a considerably smaller vicinal coupling constant ($^3J_{2,3}$ = 4–5 Hz). Protons at C^2/C^3, C^1/C^4, and C^5/C^6 in compounds **IVc** and **IVd** are equivalent in pairs. Protons of the methylene bridge, *syn*-7-H and *anti*-7-H in the spectra of all compounds resonate as doublets at δ 1.20–1.35 ppm with a coupling constant of 9–10 Hz. In addition, signals from the amide NH proton and from protons in the pyridine ring (δ 7.03–8.20 ppm) were present.

The UV spectra of compounds **IIIa**, **IIIb**, **IVa**, **IVb**, **Va**, and **Vb** are consistent with their structure and, in keeping with the data of [6] (where the reactivity of aminopyridines was studied), indicate that compounds **III** exist mainly in the amino form and that their reactions with electrophiles involve the exocyclic nitrogen atom.

The observed regioselectivity follows from the electron density distribution in molecules **IIIa**–**IIIg**, which was determined previously (in 1970s) for some compounds of this series. Table 1 contains proton affinities of the nitrogen atoms in compounds **IIIa**–**IIIg**, which were calculated by the PM3 semiempirical method [11]. In all compounds, except for **IIId**, the proton affinities of the endocyclic nitrogen atoms are greater than those of the amino nitrogen atom. The smallest difference was found for 2-aminopyridine and 2-amino-5-iodopyridine (2.3 kcal/mol), and the largest, for 4-aminopyridine (14.0 kcal/mol). The proton affin-

Scheme 2.



A

Table 1. Energy parameters of occupied molecular orbitals and orbital coefficients[a] in molecules **IIIa**–**IIIg** (PM3 calculations)

Comp. no.	Proton affinity, kcal/mol		HOMO		II-OMO	
	N^1	NH_2	*E*, eV	orbital coefficients, %	*E*, eV	orbital coefficients, %
IIIa	199.8	197.5	–8.833	7.63 (N^1), 8.55 (C^2), 15.65 (C^3), 19.39 (C^5), 41.89 (NH_2)	–10.284	72.78 (N^1), 6.42 (C^2), 5.29 (C^5)
IIIb	202.3	194.6	–8.896	13.47 (C^2), 12.30 (C^3), 9.04 (C^4), 17.13 (C^6), 41.34 (NH_2)	–10.119	73.96 (N^1), 5.16 (C^2), 5.53 (C^5)
IIIc	205.9	191.9	–9.103	15.66 (N^1), 12.65 (C^3), 9.62 (C^4), 12.64 (C^5), 45.21 (NH_2)	–10.071	23.42 (C^2), 26.58 (C^3), 26.60 (C^5), 23.41 (C^6) [75.42 (N^1) in III-OMO (–10.110)]
IIId	200.7	203.4	–8.971	14.06 (C^2), 18.36 (C^3), 13.53 (C^5), 10.58 (C^6), 31.36 (NH_2), 6.73 (O)	–10.120	25.67 (N^1), 12.87 (NH_2), 8.79 (O), 9.34 (C^3), 27.21 (C^4), 10.65 (C^6) [72.77 (N^1) in IV-OMO (–10.433)]
IIIe	199.3	197.0	–8.685	33.61 (I), 5.01 (N^1), 14.09 (C^5), 7.06 (C^2), 9.01 (C^3), 23.77 (NH_2)	–9.405	97.47 (I)[57.26 (I), 25.32 (NH_2) in III-OMO (–9.686)] [72.36 (N^1) in IV-OMO (–10.467)]
IIIf	206.8	199.1	–8.591	5.07 (C^4), 12.47 (C^5), 21.16 (C^6), 5.05 (C^8), 8.01 (C^{10}), 30.23 (NH_2)	–9.412	7.60 (N^1), 25.13 (C^4), 19.33 (C^9), 12.67 (C^3) [72.06 (N^1) in III-OMO (–10.118)]
IIIg	199.5, 200.2	196.9	–8.777	7.57 (C^2), 20.76 (C^6), 11.69 (C^7), 11.75 (C^{10}), 34.17 (NH_2)	–9.716	27.46 (C^8), 17.17 (C^9), 15.02 (C^5), 11.63 (C^6), 13.78 (C^3), 5.16 (N^1), 5.39 (N^4) [34.79 (N^1), 34.53 (N^4) in III-OMO (–9.993)]

[a] NH_2 stands for the amino nitrogen atom.

ity of the oxygen atom in the hydroxy group of **IIId** is considerably lower (153.9 kcal/mol), as compared to the nitrogen atoms. Analysis of the charge distribution also indicates negative charge localization on the pyridine nitrogen atoms. Isomeric aminopyridines are characterized by fairly similar charges on the exocyclic nitrogen atom (0.08–0.09 a.u.); the charges on the ring nitrogen atom are considerably greater, but they differ only slightly for 2- and 4-aminopyridines. The largest negative charge is localized on the hydroxy oxygen atom in molecule **IVd**.

In addition, Table 1 contains the calculated energies of occupied molecular orbitals and the corresponding orbital coefficients of some atoms in molecules **IIIa**–**IIIg**. The highest occupied molecular orbital (HOMO) in all these compounds is localized on the amino group (23.77–45.21%); the contribution of the later is the largest in aminopyridine molecules (41.34–45.21%), and the smallest, in 2-amino-5-iodopyridine (**IIIe**). The iodine atom in the latter is characterized by orbital coefficients of 33.61, 97.47, and 57.26% in the HOMO, II-OMO, and III-OMO, respectively. The endocyclic nitrogen atom contributes most to the II-OMO (73–74% for 2- and 3-aminopyridines), III-OMO (4-aminopyridine and compounds **IIIf** and **IIIg**), and IV-OMO (**IIId**, **IIIe**). The contribution of the ring nitrogen atom to the HOMO of 2- and 4-aminopyridines is small (7.63 and 15.66%, respectively), and the HOMO of 3-aminopyridine contains no contribution of N^1.

We can conclude that the ring nitrogen atom in aminopyridines is characterized by increased proton affinity and the maximal negative charge and that the amino nitrogen atom provides the largest contribution to the HOMO, which is the crucial factor in primary overlap of frontier orbitals of the reagents. Presumably, the examined reactions of aminopyridines with endic anhydride are orbital-controlled.

Amido acids **IVa**–**IVg** were converted into the corresponding carboximides by heating in boiling acetic acid. The progress of the reactions was monitored by TLC. The IR spectra of imides **Va**–**Vg** contained absorption bands due to symmetric and antisymmetric stretching vibrations of the carbonyl groups (1785–1775 and 1730–1706 cm^{-1}), the low-frequency band

being appreciably stronger [9]. Imides having heteroaromatic =C–H bonds and unsaturated fragments gave rise to absorption in the regions 1515–1510 and 850–720 cm^{-1}. Stretching vibrations of the strained double C=C bond (1575–1550 cm^{-1}) were not observed because of high molecular symmetry [10].

The ^1H NMR spectra of imides **Va**–**Vg** are fairly simple due to high molecular symmetry. The olefinic protons 5-H and 6-H in **Va**–**Vg** are deshielded as compared to those in norbornene ($\Delta\delta$ = 0.2–0.3 ppm) due to the presence of two electron-acceptor substituents in the bicyclic fragment; their chemical shifts are similar to the chemical shifts of the corresponding protons in endic anhydride (δ 6.32 and 6.30 ppm). Higher electronegativity of the anhydride moiety, as compared to imide, is reflected primarily in the position of signals from 2-H and 3-H, and also of the bridgehead 1-H and 4-H protons. In the ^1H NMR spectra of imides **V** we observed no coupling between 2-H and 3-H; therefore, considerable difficulties were encountered while distinguishing between their signals and those of the bridgehead protons. The signals were assigned on the basis of the results of quantum-chemical calculations of ^1H and ^{13}C chemical shifts (Table 2), which were performed for compounds **IVa**, **Va**, **Vc**, and **VIa** by the GIAO (B3LYP/6-31G**) method [12]. According to the calculations, the 2-H/3-H and C^2/C^3 signals of compounds **IVa** and **VIa** should appear in a weaker field relative to the 1-H/4-H and C^1/C^4 signals, respectively, while the corresponding signals of imides **Va** and **Vc** should be arranged in the reverse order.

Carboximides **V** were subjected to epoxidation at the strained double bond by treatment with peroxyformic acid which was used previously for oxidation of other carboximides [13]. Peroxyformic acid was prepared *in situ* from 98% formic acid and 50% hydrogen peroxide. In all cases, successful application of peroxyformic acid was ensured by its high acidity and reactivity as electrophile and oxidant, as well as by specific properties of the imide substrates having two electron-acceptor substituents which appreciably reduce nucleophilic reactivity of unsaturated compounds. These substituents destabilize intermediate cationic species, thus preventing rearrangement process which could accompany reactions of olefins with peroxyformic acid [14]. Despite the presence of oxygen and nitrogen nucleophilic centers, reactions of imides **Va**, **Vb**, and **Vd**–**Vg** with peroxyformic acid involved only the olefinic double bond, and the oxidation products were epoxy derivatives **VIa**, **VIb**, and **VId**–**VIg** which were isolated in 47–81% yield. Presumably, the following two factors are responsible for the observed chemoselectivity in the oxidation of imides **V** with peroxyformic acid. The first of these is strained character of the double bond [10], and the second is protonation of the highly basic pyridine nitrogen atoms with excess formic acid.

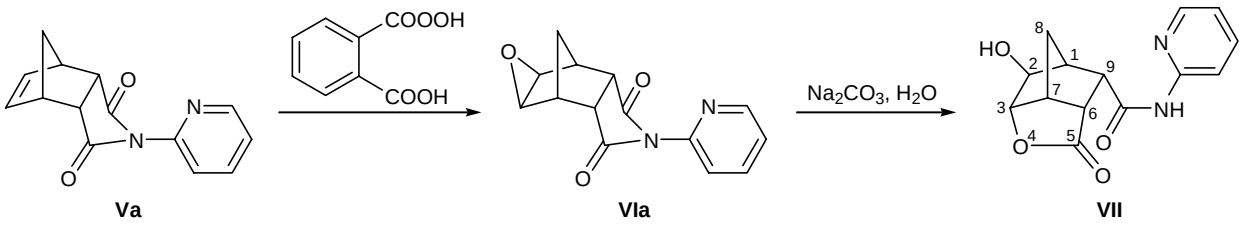
Table 2. ^1H and ^{13}C chemical shifts in the NMR spectra of compounds **IVa**, **Va**, **Vc**, and **VIa**, calculated by the GIAO method (B3LYP/6-31G** approximation)

Atom	Chemical shifts δ or δ_C, ppm			
	IVa	**Va**	**Vc**	**VIa**
N^1	3.4	3.3	3.3	2.9
N^2	3.9	3.1	3.1	2.9
3-H	3.7	3.2	3.1	3.0
4-H	3.0	3.3	3.4	2.8
5-H	6.8	6.5	6.6	3.1
6-H	6.9	6.5	6.5	3.1
syn-7-H	1.8	1.7	1.7	1.8
anti-7-H	1.4	1.4	1.4	0.8
C^1	49.8	49.2	49.6	44.0
C^2	55.1	49.1	48.6	49.7
C^3	57.6	49.2	48.6	49.7
C^4	48.4	48.9	49.8	43.7
C^5	132.5	132.6	131.8	48.8
C^6	132.3	131.3	132.1	48.8
C^7	53.6	49.1	53.7	32.0

In order to estimate the chemoselectivity in the oxidation of imide **Va** we calculated the energy and structure of its occupied molecular orbitals by the PM3 method [11]. The results showed that the highest molecular orbital in **Va** is localized by 87% on the C^5 and C^6 atoms; obviously, this is the reason why peroxy acids react at the double bond to give oxirane derivative.

The structure of the oxidation products was confirmed by the IR and ^1H and ^{13}C NMR data. The IR spectrum of **VIa**, as well as of the other imide derivatives, contained carbonyl absorption bands at 1770 and 1720 cm^{-1} and a characteristic band at 850 cm^{-1} due to stretching vibrations of the oxirane C–O bond [15]. Like parent imides, epoxy derivatives **VI** are characterized by a high molecular symmetry which complicates signal assignment in their ^1H and ^{13}C NMR spectra. The spectra were analyzed with the use of quantum-chemical calculation data (Table 2). Unlike imides **Va** and **Vb**, the 5-H and 6-H protons resonate in a stronger field (δ 3.30 ppm), and signals from the

Scheme 3.



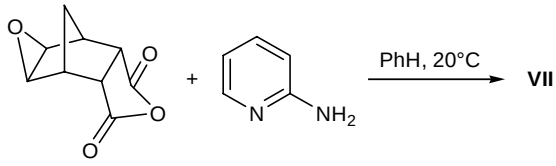
Va **VIa** **VII**

other protons in the bicyclic skeleton are also displaced upfield. The same also applies to protons of the bridging methylene group, *syn*-7-H and *anti*-7-H; the difference in the chemical shifts between the latter increases in going from imides **Va** and **Vb** to epoxy derivatives **VIa** and **VIb**. The *anti*-7-H signal is displaced upfield due to magnetically anisotropic properties of the oxirane ring (this proton is located directly above the oxirane ring plane). Considerable nonequivalence of the 7-H protons together with upfield shift of the signal from one of these indicates *exo* orientation of the epoxy fragment. The positions of signals from the pyridine fragment did not change. This means that this fragment was not involved in oxidation with peroxyformic acid. Otherwise (in the case of formation of N→O group), the corresponding signals should be displaced downfield.

By analysis of the ^{13}C NMR spectra we succeeded in distinguishing between imide **Va**, on the one hand, and amido acid **IVa** and epoxy derivative **VIa**, on the other. The ^{13}C NMR spectra of isomeric carboximides **Va** and **Vb** were fairly similar. Amido acid **IVa** displayed signals from nonequivalent carbonyl carbon atoms and C^5 and C^6. In the spectrum of **VIa**, the C^5 and C^6 signals appeared in a stronger field (δ_C 48.9 ppm); the bridging carbon signal (C^7) was also displaced upfield (δ_C 29.3 ppm) relative to the corresponding signal of imide **Va**. These data are consistent with published data for other substituted epoxynorbornanes [16].

In the epoxidation of *N*-(2-pyridyl)bicyclo[2.2.1]-hept-5-ene-*endo*-2,*endo*-3-dicarboximide (**Va**) with monoperoxyphthalic acid (generated *in situ* from phthalic anhydride and 35%hydrogen peroxide) we isolated different products, depending on the mode of treatment of the reaction mixture. Column chromatography on aluminum oxide afforded epoxy imide **VIa**, while treatment of the mixture with a solution of sodium carbonate gave an unexpected product, hydroxy lactone **VII** (Scheme 3). Compound **VII** was obtained by us previously by reaction of epoxy anhydride **VIII** with 2-aminopyridine (**IIIa**) according to the procedure described in [17] (Scheme 4). In the IR spectrum of lactone **VII** we observed absorption bands at 3440, 1779, 1689, 1530, and 1256 cm^{-1} due to vibrations of the hydroxy group, lactone carbonyl group, amide carbonyl group, N–H bond (bending vibrations), and amide C–N bond, respectively [9].

Scheme 4.



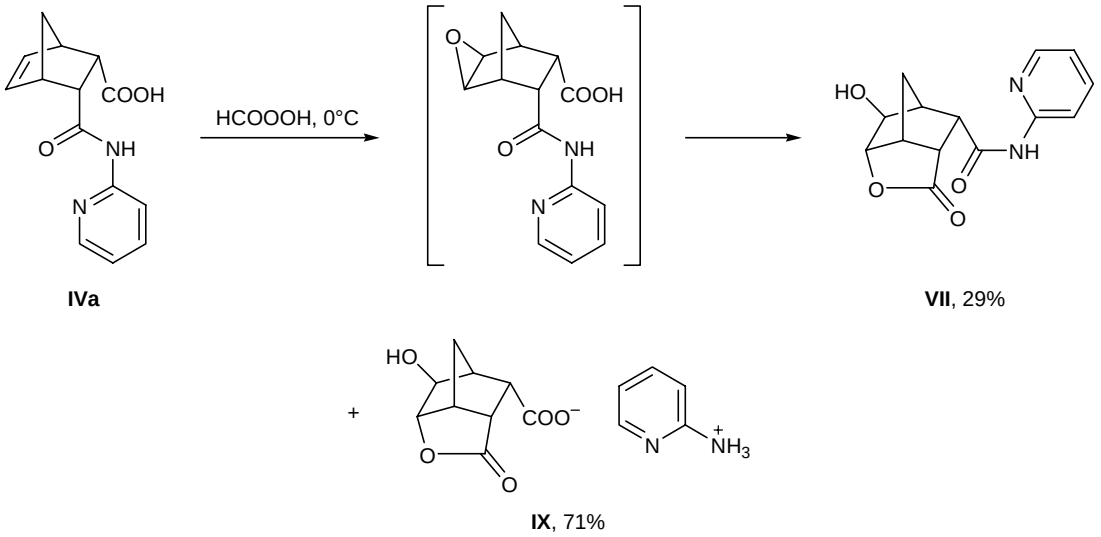
VIII

Unlike epoxy imide **VIa**, the ^1H NMR spectrum of hydroxy lactone **VII** contained no signals in the region of δ 3.30 ppm (oxirane ring protons) but contained a signal at δ 5.15 ppm from the hydroxy proton and two quite characteristic signals, a doublet at δ 4.35 ppm ($^3J_{3,7}$ = 4.4 Hz) and a singlet at δ 4.24 ppm, which belong to 3-H and 2-H, respectively.

Analogous reactions of amido acids were not the subject of a special study. Epoxidation of amido acid **IVa** with peroxyformic acid at 0°C gave a mixture of lactone **VII** and 2-pyridylammonium salt **IX**, the latter prevailing (according to the ^1H NMR data; Scheme 5). The corresponding tricyclic acid was reported previously. We failed to separate the product mixture into individual compounds, for its components were poorly soluble in most organic solvents but readily soluble in water.

Despite general similarity, the ^1H NMR spectra of **VII** and **IX** show some differences: signal of the ammonium protons in **IX** appears at δ 8.16 ppm against δ 10.64 ppm for the amide proton in **VII**, and all signals in the spectrum of salt **IX** are displaced upfield relative to those of amido lactone **VII**. Presumably, the carboxy and carboxamide groups in amido acid **IVa** compete with each other in the intramolecular cyclization of intermediate epoxy derivative.

Scheme 5.



IVa **VII**, 29%

IX, 71%

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord 75IR spectrometers from samples prepared as KBr pellets. The UV spectra were measured in the λ range from 200 to 350 nm on a Specord UV-Vis spectrophotometer from solutions in ethanol (c = 10^{-4} M, d = 1 cm). The ^{1}H NMR spectra were obtained on Varian VXR (200 or 300 MHz) and Inova 400 instruments (400 MHz) from solutions in DMSO-d_6 and CD_3OD using TMS as internal reference. The ^{13}C NMR spectra were measured on an Inova 400 spectrometer at 100.57 MHz. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether and 2-propanol as eluent; spots were visualized by treatment with iodine vapor. The elemental compositions were determined on a Carlo Erba analyzer.

Reaction of bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride (II) with amines IIIa–IIIg (*general procedure*). Amine **IIIa**–**IIIg**, 0.02 mol, was added under stirring to a solution of 3.28 g (0.02 mol) of anhydride **II** in 10–15 ml of anhydrous benzene, and the mixture was stirred at room temperature until the reaction was complete (TLC). The precipitate was filtered off, washed with benzene on a filter, and dried in air.

***endo*-3-(2-Pyridylcarbamoyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVa).** Yield 4.46 g (86%), mp 147–149°C. IR spectrum, ν, cm^{-1}: 3210, 3130, 3034, 1710, 1680, 1582, 1434, 1334, 1252, 722. UV spectrum, λ_{max}, nm (log ε): 243 (4.23), 283 (3.93). ^{1}H NMR spectrum, δ, ppm: 11.68 s (1H, COOH); 10.32 s (1H, NH); 8.26, 7.96, 7.78, 7.02 (4H, H_{arom}); 6.17 m (1H, 5-H); 6.06 m (1H, 6-H, $^3J_{5,6}$ = 5.5, $^3J_{4,5}$ = $^3J_{6,1}$ = 3.1 Hz); 3.49 m (1H, 2-H); 3.24 m (1H, 3-H, $^3J_{2,3}$ = 10.4, $^3J_{2,1}$ = $^3J_{3,4}$ = 3.2 Hz); 3.07 m (1H, 1-H); 3.01 m (1H, 4-H); 1.18 d (1H, *syn*-7-H); 1.17 d (1H, *anti*-7-H, $^2J_{7,7}$ = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 178.9 (C=O), 178.8 (C=O), 135.9 (C^5, C^6), 51.4 (C^7), 46.3 (C^1, C^4), 46.0 (C^2), 45.9 (C^3). Found, %: C 65.14; H 5.46; N 10.81. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.12; H 5.43; N 10.85.

***endo*-3-(3-Pyridylcarbamoyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVb).** Yield 4.36 g (84%), mp 187–189°C. IR spectrum, ν, cm^{-1}: 3276, 3130, 3038, 1710, 1690, 1588, 1422, 1334, 1252, 702. UV spectrum, λ_{max}, nm (log ε): 246 (4.15), 286 (3.54). ^{1}H NMR spectrum, δ, ppm: 11.60 s (1H, COOH); 9.90 s (1H, NH); 8.65, 8.20, 7.90, 7.25 (4H, H_{arom}); 6.18 m (1H, 5-H); 6.08 m (1H, 6-H); 3.48 m (1H, 2-H); 3.27 m (1H, 3-H); 3.09 m (1H, 1-H); 3.02 m (1H, 4-H); 1.35 d (1H, *syn*-7-H); 1.22 d (1H, *anti*-7-H). Found, %: C 65.05; H 5.48; N 10.91. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.12; H 5.43; N 10.85.

***endo*-3-(4-Pyridylcarbamoyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVc).** Yield 2.58 g (50%), mp 195–197°C. IR spectrum, ν, cm^{-1}: 3352, 3178, 3030, 1730, 1640, 1586, 1438, 1338, 1276, 832, 726. ^{1}H NMR spectrum, δ, ppm: 10.31 s (1H, COOH), 7.99 and 6.51 (4H, H_{arom}), 6.33 s (1H, NH), 6.08 m (2H, 5-H, 6-H), 3.12 m (2H, 2-H, 3-H), 3.00 m (2H, 1-H, 4-H), 1.24 d (1H, *syn*-7-H), 1.15 d (1H, *anti*-7-H, $^2J_{7,7}$ = 8.4 Hz). Found, %: C 65.20; N 5.39; N 10.90. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.12; N 5.43; N 10.85.

***endo*-3-(3-Hydroxy-2-pyridylcarbamoyl)bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVd).** Yield 3.29 g (60%), mp 154–156°C. IR spectrum, ν, cm^{-1}: 3425, 3325, 3020, 1695, 1640, 1590, 1425, 1380, 1270, 740. ^1H NMR spectrum, δ, ppm: 7.35, 6.80, 6.35 (3H, H_{arom}); 6.10 m (2H, 5-H, 6-H); 5.10 s (1H, OH); 3.12 m (2H, 2-H, 3-H); 3.03 m (2H, 1-H, 4-H); 1.35 d (1H, *syn*-7-H); 1.28 d (1H, *anti*-7-H, $^2J_{7,7}$ = 9.7 Hz). Found, %: C 61.39; H 5.10; N 10.33. $C_{14}H_{14}N_2O_4$. Calculated, %: C 61.31; H 5.11; N 10.22.

***endo*-3-(5-Iodo-2-pyridylcarbamoyl)bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVe).** Yield 6.80 g (89%), mp 219–220°C. IR spectrum, ν, cm^{-1}: 3250, 3045, 1722, 1710, 1612, 1585, 1545, 1482, 1380, 1192, 1020, 740. ^1H NMR spectrum, δ, ppm: 11.70 s (1H, COOH); 10.50 s (1H, NH); 8.48, 8.03, 7.85 (3H, H_{arom}); 6.15 m (1H, 5-H); 6.07 m (1H, 6-H, $^3J_{5,6}$ = 5.6, $^3J_{4,5}$ = $^3J_{6,1}$ = 2.4 Hz); 3.48 m (1H, 2-H); 3.42 m (1H, 3-H, $^3J_{2,3}$ = 10.4, $^3J_{2,1}$ = $^3J_{3,4}$ = 3.3 Hz); 3.27 m (1H, 1-H); 3.22 m (1H, 4-H); 1.30 d (1H, *syn*-7-H); 1.25 d (1H, *anti*-7-H, $^2J_{7,7}$ = 8.6 Hz). Found, %: C 43.69; H 3.45; N 7.35. $C_{14}H_{13}IN_2O_3$. Calculated, %: C 43.75; H 3.39; N 7.29.

***endo*-3-(6-Quinolylcarbamoyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVf).** Yield 5.78 g (94%), mp 195–197°C. IR spectrum, ν, cm^{-1}: 3295, 3160, 3010, 1710, 1645, 1570, 1530, 1370, 1275, 1220, 720. Found, %: C 70.04; H 5.15; N 10.01. $C_{18}H_{16}N_2O_3$. Calculated, %: C 70.13; H 5.19; N 9.09.

***endo*-3-(6-Quinoxalylcarbamoyl)bicyclo[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IVg).** Yield 6.01 g (97%), mp 161–162°C. IR spectrum, ν, cm^{-1}: 3312, 3285, 3020, 1725, 1710, 1635, 1600, 1560, 1520, 1440, 1265, 1210, 1048, 720. ^1H NMR spectrum, δ, ppm: 11.73 s (1H, COOH); 8.85, 8.77, 8.43 (3H, H_{arom}); 8.31 s (1H, NH); 8.00, 7.86 (2H, H_{arom}); 6.23 m (1H, 5-H); 6.11 m (1H, 6-H); 3.46 m (1H, 2-H); 3.43 m (1H, 3-H); 3.14 m (1H, 1-H); 3.05 m (1H, 4-H); 1.38 d (1H, *syn*-7-H); 1.31 d (1H, *anti*-7-H, $^2J_{7,7}$ = 6.8 Hz). Found, %: C 66.10; H 4.91; N 13.50. $C_{17}H_{15}N_3O_3$. Calculated, %: C 66.02; H 4.85; N 13.59.

Bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximides Va–Vg (*general procedure*). A solution of 2 mmol of amido acid **IVa**–**IVg** in 10–15 ml of glacial acetic acid was heated under reflux until the reaction was complete (6–10 h, TLC). The solvent was removed under reduced pressure, 5–7 ml of water was added to the residue, and the precipitate was filtered off, dried, and recrystallized from 2-propanol.

***N*-(2-Pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Va).** Yield 0.38 g (80%), mp 171–173°C. IR spectrum, ν, cm^{-1}: 3039, 1776, 1704, 1487, 1338, 1176, 845, 705. UV spectrum, λ_{max}, nm (log ε): 227 (4.16), 267 (3.78). ^1H NMR spectrum, δ, ppm: 8.58, 8.36, 7.61, 7.52 (4H, H_{arom}); 6.26 m (2H, 5-H, 6-H); 3.54 m (2H, 1-H, 4-H); 3.35 m (2H, 2-H, 3-H); 1.61 m (2H, *syn*-7-H, *anti*-7-H). ^{13}C NMR spectrum, δ_C, ppm: 177.1 (C=O); 149.7, 148.2, 135.4, 129.6, 124.6 (C_{arom}); 135.2 (C^5, C^6); 52.5 (C^7); 46.4 (C^1, C^4); 45.6 (C^2, C^3). Found, %: C 69.91; H 5.08; N 11.71. $C_{14}H_{12}N_2O_2$. Calculated, %: C 70.00; H 5.00; N 11.67.

***N*-(3-Pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Vb).** Yield 0.34 g (71%), mp 167–169°C. IR spectrum, ν, cm^{-1}: 3458, 3040, 1776, 1706, 1378, 1177, 706. UV spectrum: λ_{max} 265 nm (log ε 3.51). ^1H NMR spectrum, δ, ppm: 8.51, 8.36, 7.67, 7.50 (4H, H_{arom}); 6.25 m (2H, 5-H, 6-H); 3.53 m (2H, 1-H, 4-H); 3.40 m (2H, 2-H, 3-H); 1.73 d (1H, *syn*-7-H); 1.65 d (1H, *anti*-7-H, $^2J_{7,7}$ = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 177.1 (C=O); 148.5, 147.0, 135.3, 129.7, 124.2 (C_{arom}); 134.6 (C^5, C^6); 52.1 (C^7); 46.2 (C^1, C^4); 45.6 (C^2, C^3). Found, %: C 70.06; H 5.03; N 11.61. $C_{14}H_{12}N_2O_2$. Calculated, %: C 70.00; H 5.00; N 11.67.

***N*-(4-Pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Vc).** Yield 0.38 g (80%), mp 150–152°C. IR spectrum, ν, cm^{-1}: 1785, 1715, 1515, 1350, 1180, 720. ^1H NMR spectrum, δ, ppm: 8.02 and 6.63 (4H, H_{arom}), 6.10 m (2H, 5-H, 6-H), 3.10 m (2H, 1-H, 4-H), 3.05 m (2H, 2-H, 3-H), 1.28 d (1H, *syn*-7-H); 1.20 d (1H, *anti*-7-H). Found, %: C 70.08; H 4.96; N 11.65. $C_{14}H_{12}N_2O_2$. Calculated, %: C 70.00; H 5.00; N 11.67.

***N*-(3-Hydroxy-2-pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Vd).** Yield 0.33 g (65%), mp 269–271°C. IR spectrum, ν, cm^{-1}: 3040, 1785, 1730, 1595, 1480, 1395, 1350, 1200, 1175, 730. ^1H NMR spectrum, δ, ppm: 9.85 s (1H, OH); 7.90, 7.26, 7.18 (3H, H_{arom}); 6.18 m (2H, 5-H, 6-H); 3.42 m (2H, 1-H, 4-H); 3.35 m (2H, 2-H, 3-H); 1.68 d (1H, *syn*-7-H); 1.60 d (1H, *anti*-7-H, $^2J_{7,7}$ = 8.0 Hz). Found, %: C 65.71; H 4.73; N 11.06. $C_{14}H_{12}N_2O_3$. Calculated, %: C 65.63; H 4.69; N 10.94.

***N*-(5-Iodo-2-pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Ve).** Yield 0.40 g (54%), mp 156–157°C. IR spectrum, ν, cm^{-1}: 3015, 1790, 1730, 1580, 1475, 1390, 1350, 1190, 745.

Found, %: C 45.95; H 2.99; N 7.59. $C_{14}H_{11}IN_2O_2$. Calculated, %: C 45.90; H 3.01; N 7.65.

***N*-(6-Quinolyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Vf).** Yield 0.54 g (93%), mp 209–211°C. IR spectrum, ν, cm^{-1}: 3020, 1785, 1730, 1518, 1390, 1190, 725. Found, %: C 74.55; H 4.94; N 9.72. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.48; H 4.83; N 9.66.

***N*-(6-Quinoxalyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (Vg).** Yield 0.43 g (75%), mp 226.5–228°C. IR spectrum, ν, cm^{-1}: 3025, 1780, 1722, 1515, 1392, 1195, 728. Found, %: C 70.03; H 4.51; N 14.38. $C_{17}H_{13}N_3O_2$. Calculated, %: C 70.10; H 4.47; N 14.43.

Oxidation of bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximides Va, Vb, and Vd–Vg with peroxyformic acid (*general procedure*). Bicyclo-[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide **Va**, **Vb**, or **Vd–Vg**, 2 mmol, was dissolved in 8–10 ml of 98% formic acid, 4 mmol of 50% hydrogen peroxide was added dropwise under stirring, and the mixture was stirred at room temperature until the reaction was complete (3–7 days, TLC). Volatile compounds were removed under reduced pressure, and the residue was purified by recrystallization from 2-propanol or ethyl acetate.

***exo*-5,6-Epoxy-*N*-(2-pyridyl)bicyclo[2.2.1]heptane-*endo*-2,*endo*-3-dicarboximide (VIa).** Yield 0.37 g (71%), mp 176–178°C. IR spectrum, ν, cm^{-1}: 3040, 1770, 1720, 1500, 1370, 850. ^{1}H NMR spectrum, δ, ppm: 8.38 (1H, H_{arom}), 7.54 (1H, H_{arom}), 7.46 (1H, H_{arom}), 3.39 m (2H, 5-H, 6-H), 2.98 m (2H, 2-H, 3-H), 2.30 m (2H, 1-H, 4-H), 1.41 d (1H, *syn*-7-H), 1.15 d (1H, *anti*-7-H, $^2J_{7,7}$ = 10.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 175.2 (C=O); 140.5, 140.4, 128.1, 127.8, 126.2 (C_{arom}); 48.9 (C^5, C^6); 48.3 (C^2, C^3); 39.8 (C^1, C^4); 29.3 (C^7). Found, %: C 65.68; H 4.73; N 10.89. $C_{14}H_{12}N_2O_3$. Calculated, %: C 65.63; H 4.69; N 10.94.

***exo*-5,6-Epoxy-*N*-(3-pyridyl)bicyclo[2.2.1]heptane-*endo*-2,*endo*-3-dicarboximide (VIb).** Yield 0.32 g (63%), mp 226.5–228°C. IR spectrum, ν, cm^{-1}: 3030, 1780, 1710, 1595, 1500, 1445, 1180, 860. ^{1}H NMR spectrum, δ, ppm: 8.59, 8.35, 7.77, 7.56 (4H, H_{arom}); 3.43 m (2H, 5-H, 6-H); 3.38 m (2H, 2-H, 3-H); 2.97 m (2H, 1-H, 4-H); 1.42 d (1H, *syn*-7-H); 1.14 d (1H, *anti*-7-H, $^2J_{7,7}$ = 9.4 Hz). Found, %: C 65.70; H 4.71; N 10.85. $C_{14}H_{12}N_2O_3$. Calculated, %: C 65.63; H 4.69; N 10.94.

***exo*-5,6-Epoxy-*N*-(3-hydroxy-2-pyridyl)bicyclo-[2.2.1]heptane-*endo*-2,*endo*-3-dicarboximide (VId).** Yield 0.26 g (47%), mp 286–288°C (decomp.). IR spectrum, ν, cm^{-1}: 3050, 1792, 1732, 1585, 1480, 1320, 1205, 1190, 865. ^{1}H NMR spectrum, δ, ppm: 8.00 s (1H, OH), 7.35 (3H, H_{arom}), 3.21 m (2H, 5-H, 6-H), 2.95 m (2H, 2-H, 3-H), 2.95 m (2H, 1-H, 4-H), 1.40 d (1H, *syn*-7-H), 1.11 d (1H, *anti*-7-H, $^2J_{7,7}$ = 9.1 Hz). Found, %: C 61.82; H 4.46; N 10.41. $C_{14}H_{12}N_2O_4$. Calculated, %: C 61.76; H 4.41; N 10.29.

***exo*-5,6-Epoxy-*N*-(5-iodo-2-pyridyl)bicyclo-[2.2.1]heptane-*endo*-2,*endo*-3-dicarboximide (VIe).** Yield 0.44 g (58%), mp 148–150°C (decomp.). IR spectrum, ν, cm^{-1}: 3060, 1778, 1712, 1566, 1462, 1362, 1190, 848. Found, %: C 44.03; H 2.90; N 7.37. $C_{14}H_{11}IN_2O_3$. Calculated, %: C 43.98; H 2.88; N 7.33.

***exo*-5,6-Epoxy-*N*-(6-quinolyl)bicyclo[2.2.1]heptane-*endo*-2,*endo*-3-dicarboximide (VIf).** Yield 0.50 g (81%), mp 243–244°C. IR spectrum, ν, cm^{-1}: 3052, 1768, 1712, 1502, 1372, 1176, 854. ^{1}H NMR spectrum, δ, ppm: 8.98, 8.42, 8.12, 7.99, 7.66, 7.60 (6H, H_{arom}); 3.48 m (2H, 5-H, 6-H); 3.41 m (2H, 2-H, 3-H); 3.01 m (2H, 1-H, 4-H); 1.45 d (1H, *syn*-7-H); 1.17 d (1H, *anti*-7-H, $^2J_{7,7}$ = 10.2 Hz). Found, %: C 70.51; H 4.60; N 9.21. $C_{18}H_{14}N_2O_3$. Calculated, %: C 70.59; H 4.58; N 9.15.

***exo*-5,6-Epoxy-*N*-(6-quinoxalyl)bicyclo[2.2.1]-heptane-*endo*-2,*endo*-3-dicarboximide (VIg).** Yield 0.47 g (76%), mp 248–250°C (decomp.). IR spectrum, ν, cm^{-1}: 3070, 1770, 1712, 1504, 1380, 1180, 844. Found, %: C 66.52; H 4.31; N 13.60. $C_{17}H_{13}N_3O_3$. Calculated, %: C 66.45; H 4.23; N 13.68.

Oxidation of compound Va with monoperoxyphthalic acid. *a*. A 35% solution of hydrogen peroxide, 0.43 g (4.4 mmol), was added under stirring to a mixture of 0.53 g (2.2 mmol) of compound **Va**, 0.65 g (4.4 mmol) of phthalic anhydride, and 0.07 g (1.1 mmol) of urea in 20 ml of ethyl acetate. The mixture was stirred at room temperature until the reaction was complete (TLC) and was then passed through a column charged with aluminum oxide. The solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol. We thus isolated 0.34 g (60%) of compound **VIa**.

b. The reaction was carried out as described above in *a* with the same amounts of the reactants. When the reaction was complete, the mixture was neutralized with a saturated solution of sodium carbonate, the organic phase was separated, and the aqueous phase was washed with three portions of ethyl acetate. The extracts were combined with the organic phase, the

solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol. We thus isolated 0.24 g (40%) of *exo*-2-hydroxy-*endo*-9-(2-pyridylcarbamoyl)-4-oxatricyclo[4.2.1.$0^{3,7}$]nonan-5-one (**VII**), mp 116–118°C. IR spectrum, ν, cm^{-1}: 3440, 1779, 1689, 1530, 1256, 1193, 1157, 1015. ^1H NMR spectrum, δ, ppm: 10.69 s (1H, NH); 8.36, 8.21, 7.39, 7.14 (4H, H_{arom}); 5.15 (1H, OH); 4.35 d (1H, 3-H, $^3J_{3,7}$ = 4.4 Hz); 4.24 s (1H, 2-H); 3.60 m (1H, 6-H, $^3J_{6,9}$ = 10.9 Hz); 3.30 m (1H, 7-H); 2.78 m (1H, 9-H, $^3J_{9,1}$ = 4.1 Hz); 2.47 br.s (1H, 1-H); 2.01 d (1H, *syn*-8-H); 1.47 d (1H, *anti*-8-H, $^2J_{8,8}$ = 10.5 Hz). Found, %: C 61.35; H 5.14; N 10.27. $C_{14}H_{14}N_2O_4$. Calculated, %: C 61.31; H 5.11; N 10.22.

Oxidation of *endo*-3-(2-pyridylcarbamoyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IVa). Amido acid **IVa**, 0.52 g (2 mmol), was dissolved in 5 ml of 98% formic acid, the solution was cooled to 0°C, 0.23 ml (4 mmol) of 50% hydrogen peroxide was added under stirring, and the mixture was stirred until the reaction was complete (TLC). Formic acid was removed under reduced pressure to leave an oily substance (82%) which, according to the ^1H NMR data, was a mixture of compound **VII** (29%) and 2-pyridylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.$0^{3,7}$]nonane-*endo*-9-carboxylate (**IX**) (71%). IR spectrum, ν, cm^{-1}: 3360, 3010, 2740, 1785, 1690, 1590, 1560, 1240, 1220, 1175, 1030. ^1H NMR spectrum, δ, ppm: **VII**: 10.64 s (1H, NH); 8.30, 8.22, 7.38, 7.12 (4H, H_{arom}); 5.24 (1H, OH); 4.35 d (1H, 3-H, $^3J_{3,7}$ = 4.8 Hz); 4.29 s (1H, 2-H); 3.62 m (1H, 6-H, $^3J_{6,9}$ = 10.8 Hz); 3.25 m (1H, 7-H), 2.75 m (1H, 9-H, $^3J_{9,1}$ = 4.5 Hz); 2.48 br.s (1H, 1-H); 2.02 d (1H, *syn*-8-H); 1.46 d (1H, *anti*-8-H, $^2J_{8,8}$ = 11.4 Hz); **IX**: 8.16 (3H, H_3N^+); 8.00, 7.88, 7.77, 7.38 (4H, H_{arom}); 5.52 (1H, OH); 4.32 d (1H, 3-H, $^3J_{3,7}$ = 5.1 Hz); 4.02 s (1H, 2-H); 3.20 m (1H, 7-H); 3.04 m (1H, 6-H, $^3J_{6,9}$ = 10.7 Hz); 2.67 m (1H, 9-H, $^3J_{9,1}$ = 4.7 Hz); 2.42 br.s (1H, 1-H); 1.95 d (1H, *syn*-8-H); 1.51 d (1H, *anti*-8-H, $^2J_{8,8}$ = 11.0 Hz).

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