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Lactonation of *N*-Alkyl- and *N,N*-Dialkylamido Acids of Norbornene Series in Reactions with Performic Acid

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Abstract—Reaction products were obtained from bicyclo[2.2.1]hept-5-ene-*endo,endo*-2,3-dicarboxylic (endic) acid anhydride and ammonia, methyl-, benzyl-, dimethyl-, methylbenzyl-, dibenzyl-, diethyl-, dipropyl-, diisopropyl-, and dipentylamines. The synthesized amido acids were subjected to epoxidation by organic peracids. The structure of compounds obtained was confirmed by IR, ^{1}H and ^{13}C NMR spectra, and in some instances , by X-ray diffraction analysis.

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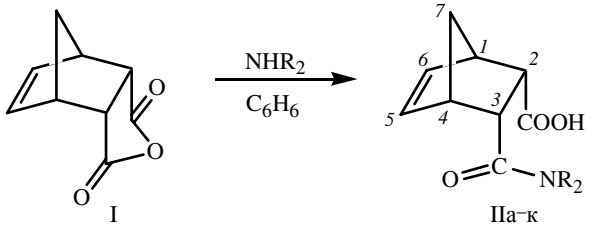
In contrast to numerous carboximides prepared with the use of bicyclo-[2.2.1]hept-5-ene-*endo*,*endo*-2,3-dicarboxylic acid anhydride (endic anhydride) (**I**), amido acids based thereon are poorly understood [1–5]. The *N*-alkylamides of bicyclo[2.2.1]hept-5-ene-*endo*,*endo*-2,3-dicarboxylic acids were successfully used in repellent compositions [6] and as agents possessing sedative action [7]. The corresponding arylamides were applied in the herbicide composition to cotton-plant protection [8], they facilitate the germination of plant seeds [9]. The spectral parameters of amido acids were not described. Known amido acids were obtained by different procedures: by heating reagents in alcohol [10], acetonitrile [11], tetrahydrofuran [12], and dimethoxyethane [8].

In the present study we investigated reactions of endic anhydride with ammonia and a series of monoalkyl- and dialkylamines (methyl-, benzyl-, dimethyl-, methylbenzyl-, dibenzyl-, diethyl-, dipropyl-, diisopropyl-, and dipentylamines).

Amido acids **IIa–IId** were described before [7, 13–16], the other compounds we obtained for the first time. Amido acids **IIa–IIj** were prepared by reaction of equimolar quantities of reagents in benzene solution at room temperature (TLC monitoring). The time of the reaction between anhydride **I** and amines depended on the structure of the latter. The synthesis of amido acids **IIa–IIe** completed within 1–2 days, the preparation of compound **IIf** required 10 days (yield 40%). Amide **IIf** was also synthesized by boiling initial reagents for 15 h (yield 69%). The reactions of anhydride **I** with diethyl-, dipropyl-, diisopropyl-, and dipentylamines continued up to two weeks. We failed to prepare amido acids from *N*-alkylanilines (*N*-methyl- and *N*-ethylaniline) both in the cold and at boiling in benzene solution for 120 h (TLC monitoring). It was established by ^{1}H NMR spectroscopy that the only reaction product was bicyclo[2.2.1]-hept-5-ene-*endo*,*endo*-2,3-dicarboxylic (endic) acid (**III**).



I IIa–к

NR_2 = NH_2 (**a**), $NHCH_3$ (**b**), $NHCH_2Ph$ (**c**), $N(CH_3)_2$ (**d**), $N(CH_3)CH_2Ph$ (**e**), $N(CH_2Ph)_2$ (**f**), $N(C_2H_5)_2$ (**g**), $N(C_3H_7)_2$ (**h**), N(*iso*-$C_3H_7)_2$ (**i**), $N(C_5H_{11})_2$ (**j**).

IR spectra of compounds **IIa–IIc** contained absorption bands in the regions 1670–1650 (CO), 1267–1252 (CN), and 3362–3280 cm^{-1} (NH), and also in the range

1770–1700 cm^{-1} characteristic of the carboxy group. In the spectra of amides **IId–IIj** the carbonyl group vibrations gave rise to bands at 1685–1625 and 1758–1690 cm^{-1}. Absorption bands belonging to the unsaturated fragments of amides **IIa–IIj** appeared in the regions 3068–3010 and 745–700 cm^{-1} corresponding to the stretching and bending vibrations of the =C–H bonds [17]. The bands of stretching vibrations of the strained double bond (1575–1550 cm^{-1}) are weak, and in the spectra of secondary amides **IIb** and **IIc** and of primary amide **IIa** they are overlapped by the band of the NH bond [18].

The structure of amido acids was confirmed by ^1H and ^{13}C NMR spectra. ^1H NMR spectra of amido acids contained all necessary signals: resonances of olefin protons H^5 and H^6 in the region 5.93–6.32 ppm, of bridgehead protons H^1 and H^4 in the range 2.86–3.05 ppm, and of protons H^2, H^3 at the carbonyl groups of the amido acids at 2.96–3.38 ppm. The latter protons in the spectra of compounds **IIb–IId** are essentially nonequivalent; their coupling corresponds to vicinal constants 10.2, 10.0, and 10.1 Hz unambiguously confirming the *exo*-orientation of these protons on the framework fragment. The signals of bridging protons H^{7s} and H^{7an} are closely located (1.11–1.35 ppm) and coupled with the constant 8.0–9.1 Hz.

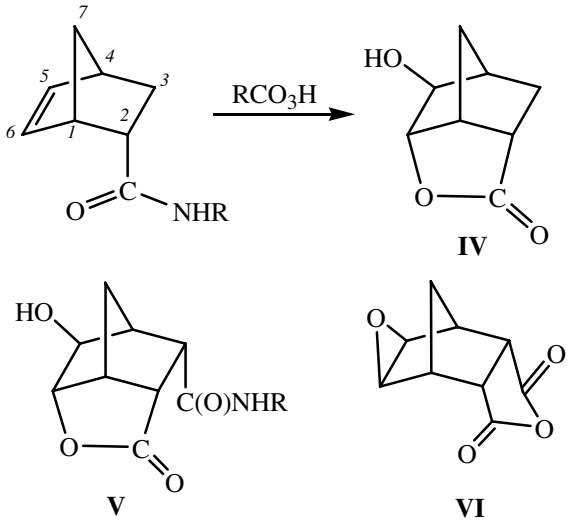
In the ^{13}C NMR spectra of amido acids **IIa** and **IIb**, like in the ^1H NMR spectra, the signals of atoms C^5 and C^6, C^1 and C^4, C^2 and C^3, and also of the carbon atoms of the carbonyl groups did not coincide (Fig. 1).

Amido acids possess several reactive sites (strained double bond, carboxy and carboxamide groups), they are capable to be converted into other class compounds involving these sites.

Unlike imides of norbornene series whose reactions with organic peracids were often described [5, 19], the oxidation of amido acids was hardly studied before. The only example concerns the oxidation of an amido acid containing a phenylethyl group where the products have not been identified [2].

The oxidation of amido acids can lead both to epoxy derivatives and to products of their heterocyclization involving the carboxy and amide groups. Such heterocyclizations of substituted norbornenes are known, in particular, lactone **IV** was obtained by epoxidation of various bicyclo-[2.2.1]hept-5-ene-2-carboxamides with the *endo*-orientation of the substituent in the presence of a large excess (4:1) of peracids [20, 21].

The formation of amidolactones **V** was observed in reactions with amines (RNH_2, R = H, Ph, CH_2Ph) of endic anhydride epoxy derivative **VI** [22]. The reactions proceeded under mild conditions in weakly alkaline medium originating from the presence of the amines.



We chose for oxidation of amido acids the performic acid that was prepared in situ from 98% formic acid and 50% water solution of hydrogen peroxide. The oxidation of amido acids **IIa, IIb, IId–IIf**, and **IIh–IIj** was carried out using double molar excess of the oxidant at 0°C (TLC monitoring). The successful application of the performic acid was underpinned by its high acidity and reactivity as an electrophilic oxidative reagent with respect to

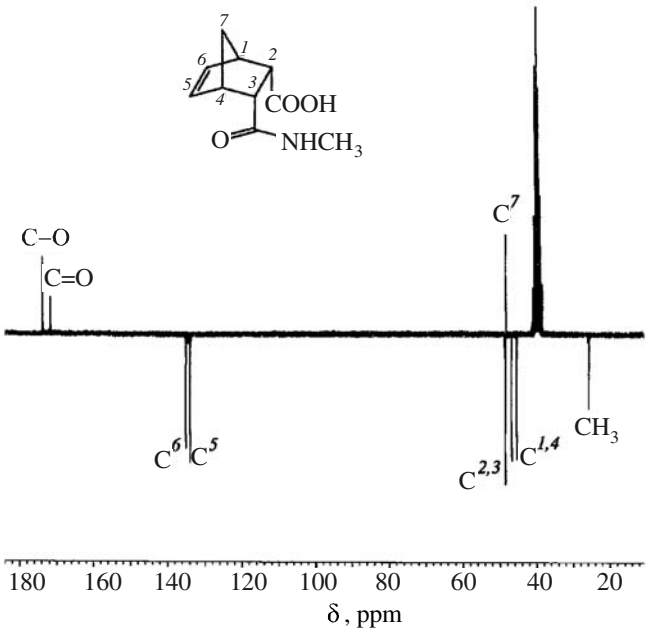


Fig. 1. ^{13}C NMR spectrum of *endo*-3-(*N*-methylcarbamoyl)-bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (**IIb**) (DMSO-d_6, 100.57 MHz).

substrates of considerably reduced nucleophilicity of the olefin due to the presence of two electron-withdrawing substituents [23].

We showed formerly [24] that oxidation of amido acids **VII** of the norbornene series with fragments of nonaromatic heterocyclic amines resulted in most cases in two types of substances: amidolactones **VIII** and salts **IX** of lactonoacid **X** with the amines contained in amide groups composition (Scheme 1).

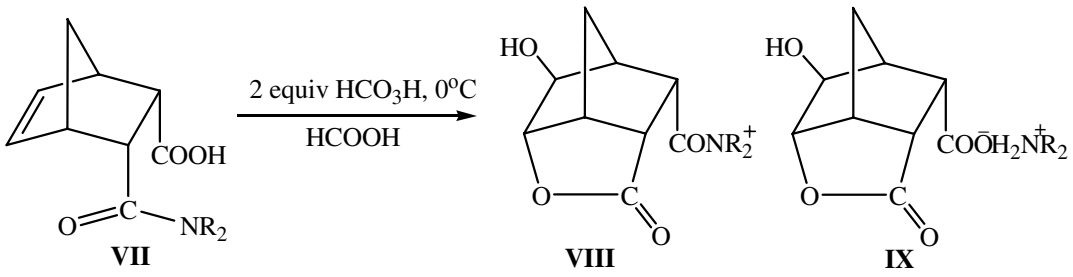
The oxidation of amido acids **IIa–IIj** also led to the formation of two types of compounds: lactonoacid **X** and salts **XI–XVI** of lactonoacid **X** with the corresponding amines (Scheme 2).

Acid **X** was previously described in [15, 20, 25]; in this study it was also prepared by known methods: It was isolated from oxidation products of endic acid (**III**) and anhydride **I**. The melting point, TLC data, and spectral behavior of compound **X** and the oxidation products obtained from amides **IIb** and **IId** were identical.

The structure of one among the typical oxidation products, salt **XVI** obtained by oxidation of amide **IIj** with performic acid, was proved by X-ray diffraction study (Fig. 2). The independent part of the unit cell contains two molecules of lactonoacid **X** (**A** and **B**) and two molecules of amine (**C** and **D**). The leveling of bond lengths O^4–C^8 and O^5–C^8 in molecules **A** and **B** {O^4–C^8 1.212(3) (**A** and **B**), O^5–C^8 1.224(3) (**A**) and 1.252(3) Å (**B**) comparable with an average bond length [26] 1.250 A in carboxylate anion}, and also the objectively revealed positions of hydrogen atoms at nitrogens in molecules **C** and **D** permit a conclusion that molecules **A** and **B** are anions which form salts with cations of dipentylammonium (**C** and **D**).

The five-membered heterocycle is in an *envelop* conformation. The deviation of C^6 atom from the mean-

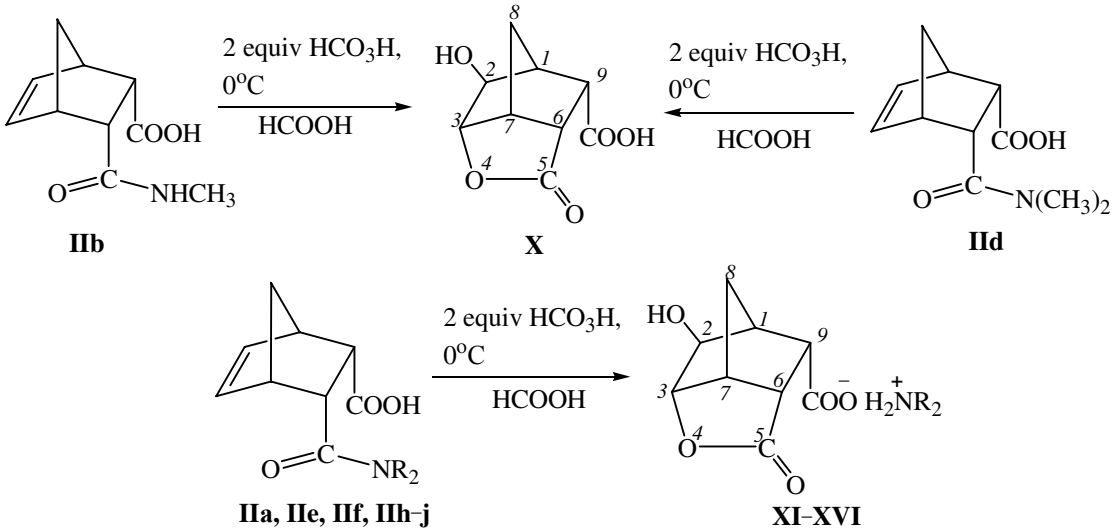
Scheme 1.



VII **VIII** **IX**

NR_2 = cycloalkyl.

Scheme 2.



IIb **X** **IId**

IIa, IIe, IIf, IIh–j **XI–XVI**

NR_2 = NH_2 (**XI**), $N(CH_3)CH_2Ph$ (**XII**), $N(CH_2Ph)_2$ (**XIII**), $N(C_3H_7)_2$ (**XIV**), N(*iso*-$C_3H_7)_2$ (**XV**), $N(C_5H_{11})_2$ (**XVI**).

square plane of the other atoms of the ring is –0.60 Å in molecule **A** and 0.66 Å in molecule **B**. The hydroxy group at C^2 atom of the bicycloheptane fragment has an *exo*-orientation, and the substituent at C^4 atom, *endo*-orientation [torsion angles $O^3C^2C^3C^4$ in molecules **A** and **B** are –179.5(2) and –178.6(2)° respectively, $C^2C^3C^4C^8$ in molecules **A** and **B** are 66.5(3) and 63.0(3)° respectively]. This position of substituents results in a shortened intramolecular contact $H^2\cdots C^8$ 2.77 Å in molecule **A** and 2.59 Å in molecule **B** (the sum of van der Waals radii is 2.87Å[27]).

In the crystal the anions and cations are bound by intermolecular hydrogen bonds O^{3a}–$H^{3aa}\cdots O^{5'b}$ (H···O 1.86 Å, O–H···O 174°), O^{3b}–$H^{3ba}\cdots O^{4'a}$ (H···O 1.89 Å, O–H···O 176°), N^{1a}–$H^{1Na}\cdots O^{5'a}$ (1 – *x*, –*y*, –*z*) (H···O 1.96 Å, N–H···O 164°), N^{1a}–$H^{1Nb}\cdots O^{5a}$ (*x*, 1 + *y*, *z*) (H···O 1.91 Å, N–H···O 155°), N^{1b}–$H^{1Nc}\cdots O^{5'b}$ (–*x*, –*y*, 1 – *z*) (H···O 1.83 Å, N–H···O 169°), N^{1b}–$H^{1Nd}\cdots O^{4b}$ (H···O 1.85 Å, N–H···O 160°).

By an example of amido acid **IIc** we studied the effect of the peracid character and the oxidation conditions on the yield of the reaction product, benzylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo[4.2.1.$0^{3,7}$]nonane-*endo*-9-carboxylate (**XVII**) (Scheme 3).

The data obtained showed an important fact: The increased amount of performic acid did not affect the yield of target product **XVII**. The replacement of the formic acid solvent by a mixture of dichloromethane and acetonitrile somewhat decreased the yield, and the use of peracetic acid instead of performic acid decelerated the oxidation and required more rigid reaction conditions.

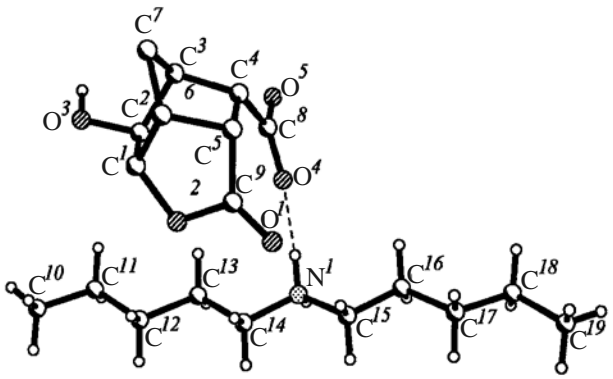
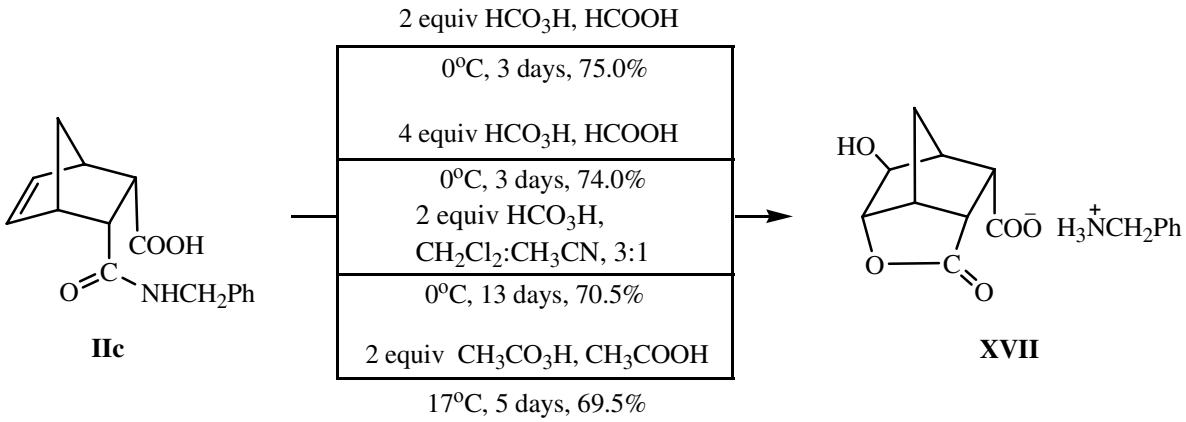


Fig. 2. Molecular structure of dipentylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo[4.2.1.$0^{3,7}$]nonane-*endo*-9-carboxylate (**XVI**) according to X-ray diffraction analysis

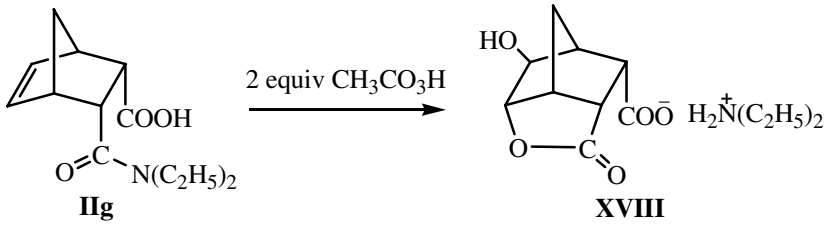
The oxidation of diethylamide **IIg** with peracetic acid prepared *in situ* yielded salt **XVIII** of lactonoacid **X** (Scheme 4). The peracetic acid was obtained in two ways: by reaction of glacial acetic acid with 50% water solution of hydrogen peroxide, and by reaction of acetic anhydride with hydrogen peroxide in chloroform in the presence

Scheme 3.



IIc **XVII**

Scheme 4.

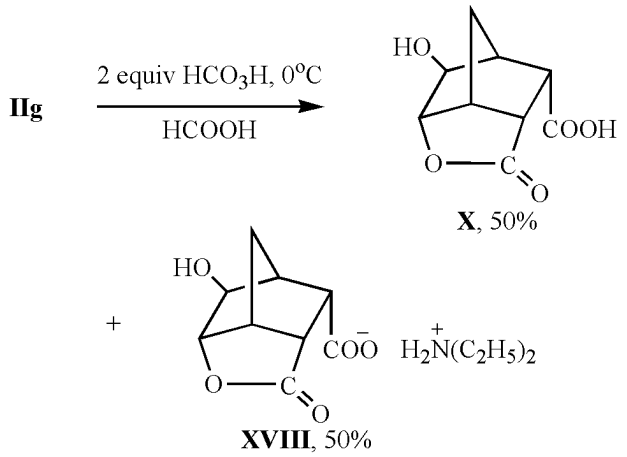


IIg **XVIII**

of sodium bicarbonate; the yield of oxidation product was 63 and 65% respectively.

The treatment of compound **IIg** with 54% *m*-chloroperbenzoic acid in dichloromethane and with freshly prepared crystalline 65% monoperoxyphthalic acid in ethyl acetate provided salt **XVIII** in 31 and 49% yield respectively. In all four cases the oxidation was carried out at room temperature using two equiv of the oxidant; the reaction time was 5, 4, 2, and 2 days respectively (TLC data).

These results were quite different from those obtained by oxidation of amide **IIg** with performic acid *in situ* in the presence of a double molar amount of the oxidant at 0°C. Under these conditions an equimolar mixture formed of lactonoacid **X** and its salt with diethylamine **XVIII** as demonstrated by ^{1}H NMR spectrum.



The structure of the oxidation product obtained from amido acid **IIg** was finally established by X-ray diffraction study on a single crystal of the compound (Figs. 3 and 4). The independent part of the unit cell of the crystal contains two molecules (**E** and **F**) and a diethylammonium cation. The bond lengths O^{4a}–C^{9a} 1.184(6), O^{5a}–C^{9a} 1.300(6), and C^{6a}–C^{9a} 1.480(7) Å in molecule **E** are comparable with the average bond lengths (1.210, 1.308, and 1.502 Å respectively) of a neutral carboxy group [26]. In molecule **F** the bond lengths O^{4c}–C^{9c} 1.223(6) and O^{5c}–C^{9c} 1.257(6) Å are closer to each other, the bond C^{6c}–C^{9c} [1.508(7) Å] is longer than in molecule **E**, and they are comparable with the bond lengths in a carboxylate anion (O^4–C^9 and O^5–C^9 1.254, C^6–C^9 1.520 Å). The above findings suggest that molecule **E** exists in the crystal in a neutral form, and molecule **F** is a carboxylate anion forming a salt with the diethylammonium cation.

The five-membered heterocycle is in an *envelop* conformation. The deviation of C^2 atom from the mean-square plane of the other atoms of the ring is –0.62 Å in molecule **E** and 0.66 A in molecule **F**. The hydroxy group at C^4 atom of the bicycloheptane fragment has an *exo*-orientation, and the substituent at C^6 atom, *endo*-orientation [torsion angles $C^2C^3C^4O^3$ in molecules **E** and **F** 107.3(4) and 108.7(5)° respectively; $C^2C^1C^6C^9$ in molecules **E** and **F** 134.2(4) and 136.5(4)° respectively]. This orientation of the carboxy group results in a shortened intramolecular contact $H^{4aa}\cdots C^{9a}$ 2.65 Å in molecule **E** and 2.70 Å in molecule **F** (the sum of van der Waals radii is 2.87 Å [27]). Therewith the carboxy group is turned with respect to the C^1–C^6 bond [torsion angle $C^1C^6C^9O^4$ in molecules **E** and **F** –21.6(8) and –35.1(6)° respectively].

In the crystal of the oxidation product of amido acid **IIg** molecule **E**, anion **F**, and diethylammonium cation are bound by intermolecular hydrogen bonds O^{3c}–

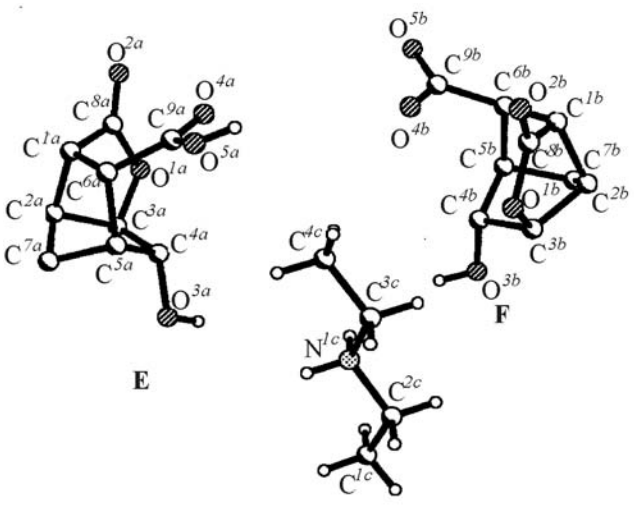


Fig. 3. Molecular structure of oxidation product obtained from amido acid **IIg** according to X-ray diffraction analysis.

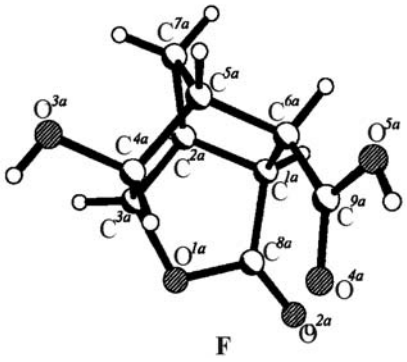


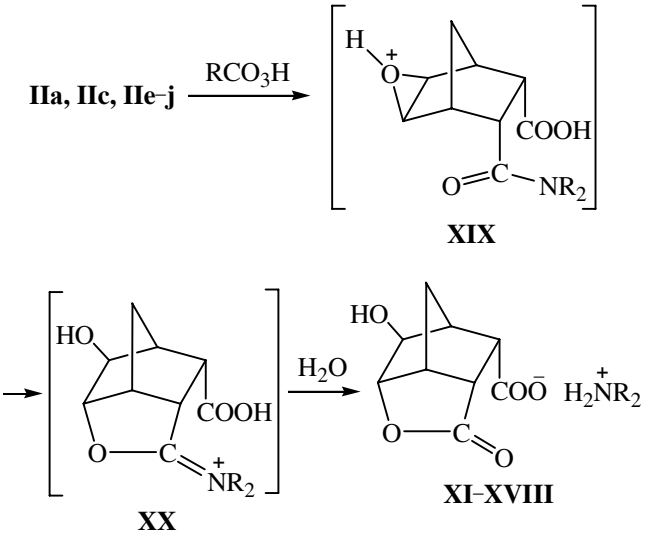
Fig. 4. Molecular structure of lactonoacid **X** according to X-ray diffraction analysis.

$H^{3cc}\cdots O^{5c'}$ (0.5 + *x*, 0.5 – *y*, 0.5 + *z*) (H···O 1.86 Å, O–H···O 172°), O^{3a}–$H^{3ac}\cdots O^{4c'}$ (0.5 + *x*, 0.5 – *y*, 0.5 + *z*) (H···O 1.81 Å, O–H···O 172°), N^{1b}–$H^{1be}\cdots O^{4a'}$ (0.5 + *x*, 0.5 – *y*, 0.5 + *z*) (H···O 1.90 Å, N–H···O 163°), N^{1c}–$H^{1bd}\cdots O^{5c'}$ (0.5 + *x*, 0.5 – *y*, 0.5 + *z*) (H···O 1.80 Å, N–H···O 173°), O^{5a}–$H^{5ac}\cdots O^{3a}$ (–0.5 + *x*, 0.5 – *y*, –0.5 + *z*) (H···O 1.82 Å, O–H···O 171°).

The structure of the other compounds was studied by IR and ^{1}H NMR spectroscopy.

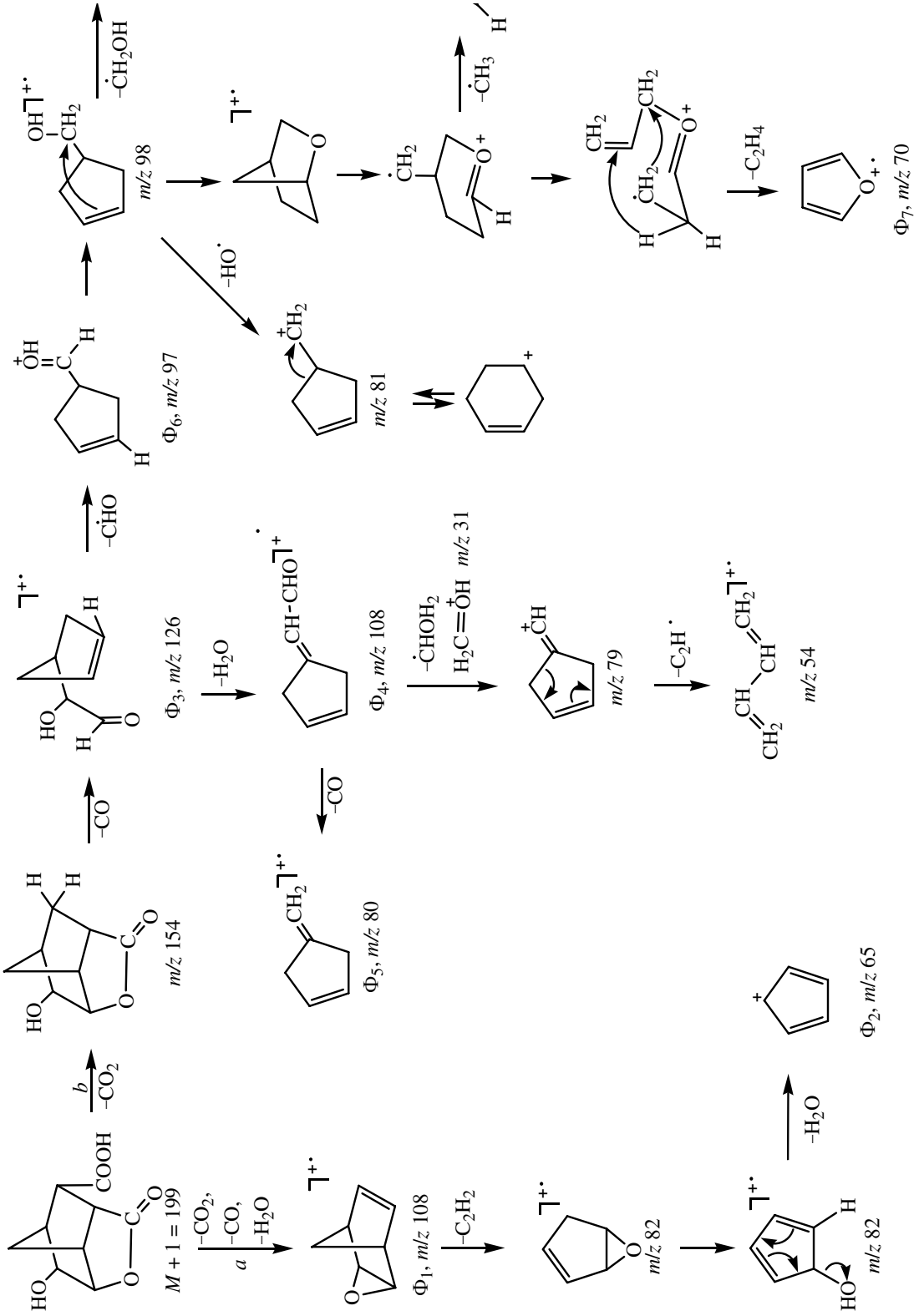
In the IR spectra of products obtained by oxidation of amido acids **IIa, IIc, IIe–IIj** and isolated as salts **XI–XVIII** the stretching vibrations of the hydroxy and ammonium groups were observed as broad bands in the regions 3415–3212 and 2650–2495 cm^{-1} ("ammonium band"); the latter in the spectra of salts **XI** and **XVII** appeared in characteristic regions 3060 and 3014 cm^{-1} respectively. A characteristic feature of the IR spectra of all the salts in question is the narrow range of frequencies (1790–1766 cm^{-1}) corresponding to the absorption of the carbonyl from the γ-lactone ring. The bands in the region 1604–1585 and 1368–1350 cm^{-1} were assigned to antisymmetric and symmetric vibrations of the carboxylate anion. The scissor bending vibrations of the latter appeared as a weak peak in the region 790–763 cm^{-1} [28]. The fragment C–O–C of the five-membered lactone ring gave rise to an absorption band in the range 1030–1014 cm^{-1} [18].

In the complex ^{1}H NMR spectra of salts **XI–XVIII** the key signals of protons H^2 and H^3 deshielded due to the neighbor oxygen-containing substituents appeared in the region 4.03–4.26 and 4.22–4.45 ppm. The first signals is a singlet, the second is a doublet because of the coupling with proton H^7 ($^3J_{3,7}$ 4.8–5.6 Hz). The *endo*-orientation of substituents attached to atoms C^6 and C^9 is revealed by the values of the vicinal coupling constants of the protons linked to this carbon atoms (10.5–10.8 Hz). The signals of the *exo*-protons at C^6 and C^9 atoms (doublets in the regions 2.48–2.64 and 2.82–3.52 ppm respectively) suffer additional splitting by the coupling with protons H^1 and H^7. It is worth mentioning that the chemical shifts of the bridgehead protons (H^1, H^7) are different since the latter is additionally included into the five-membered lactone. A crucial evidence is the presence of a signal in the region 7.35–8.47 ppm belonging to the resonance of equivalent protons attached to the ammonium nitrogen. The integral intensity of the latter signal in the ^{1}H NMR spectrum registered in $CDCl_3$ for the oxidation product obtained by treating amide **IIg** with performic acid definitely indicates equimolar ratio of the reaction products, lactonoacid **X** and salt **XVIII**. The amount of hydrogen atoms of ethyl groups in the cation part of compound **XVIII** and methylene groups in compound **XVIII** are strictly equivalent thus additionally confirming the suggested salt-like structure. The ^{1}H NMR spectrum of acid **X** in respect to the reciprocal position of signals from the framework is like the ^{1}H NMR spectra of salts **XI–XVIII**. A distinguishing feature of the acid **X** spectrum is only the lack of the signals from protons at the ammonium nitrogen and from the alkyl groups.



The decomposition under the electron impact of the product of amide **IIg** oxidation, salt **XVIII**, confirms the presence in the molecule of a lactone ring. The diethylammonium cation eliminates a proton under the electron impact transforming into diethylamine (*m/z* 73). Further the proton evidently is captured by the anion of *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylic acid contained in the composition of salt **XVIII** giving compound **X** whose decomposition during measuring the mass spectrum is shown in the scheme. The analysis of lactonoacid **X** decomposition revealed the following fragmentation routes: path *a* where the primary decomposition of the molecular ion occurred with a loss of carbon dioxide molecule, of a carbon monoxide, and water to form cation-radical Φ_1 (*m/z* 108) undergoing a series of unstable transformation to give finally cyclopentadienyl cation Φ_2 (*m/z* 65); path *b* with a loss of a carbon monoxide molecule from the molecular ion providing ion Φ_3 (*m/z* 126) that decomposed by two routes. On the one hand elimination of water and carbon monoxide resulted in formation of ions Φ_4 (*m/z* 108) and Φ_5 (*m/z* 80), on the other hand, a loss of a formyl

Scheme 5.


M + 1 = 199
m/z 154
Φ1, m/z 108
m/z 82
m/z 82
Φ2, m/z 65
Φ3, m/z 126
Φ4, m/z 108
Φ5, m/z 80
Φ6, m/z 97
m/z 98
m/z 81
m/z 79
m/z 54
Φ7, m/z 70
m/z 31
–CO2
–CO
–H2O
–C2H2
–CO2
–CO
–CHO
–H2O
–CO
–HO
–CHOH2
H2C=OH
–C2H3
–CH2OH
–H2O
–C2H4
–C2H3
a
b

radical yielded ion Φ_6 (*m/z* 97) that suffered a series of transformation on the way to dehydrofuran cation-radical Φ_7 (*m/z* 70). The processes of ions Φ_3, Φ_4, Φ_5, Φ_6, and Φ_7 formation are confirmed by the corresponding metastable transitions. The routes of other ions formation are indicated in the Scheme 5.

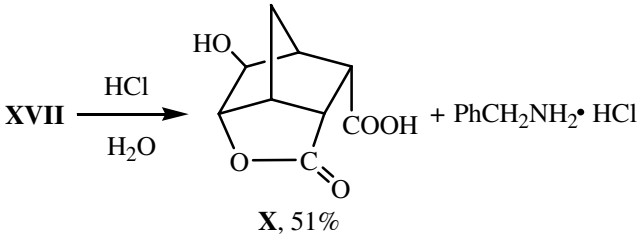
The data obtained suggested an approach to understanding the formation of salt-like products under the oxidation conditions. Salts **XI–XVIII** were obtained as a result of a nucleophilic attack by the oxygen of carboxamide group on the contiguous electrophilic carbon of the protonated epoxide **XIX** followed by hydrolysis of iminium intermediate **XX** and accompanied by transfer of a proton from the carboxy group to the amine molecule formed in hydrolysis.

Salt **XVII** was converted into lactonoacid **X** by treating the water solution of the former with an equmolar 20% hydrochloric acid. We succeeded in separating the reaction products owing to different solubility of acid **X** and benzylamine hydrochloride in hot acetone.

By an example of lactonoacid **X** and diethylamine we showed the possibility to obtain and isolate in a free state salt **XVIII**, and also the ready formation of the corresponding amidolactone **XXI** (Scheme 6). The yield of the latter was considerably higher (by 18%) in its preparation from salt **XVIII** as compared with the synthesis by successive treatment of compound **X** with diethylamine and a dichloromethane solution of dicyclohexylcarbodiimide (DCC) in the cold.

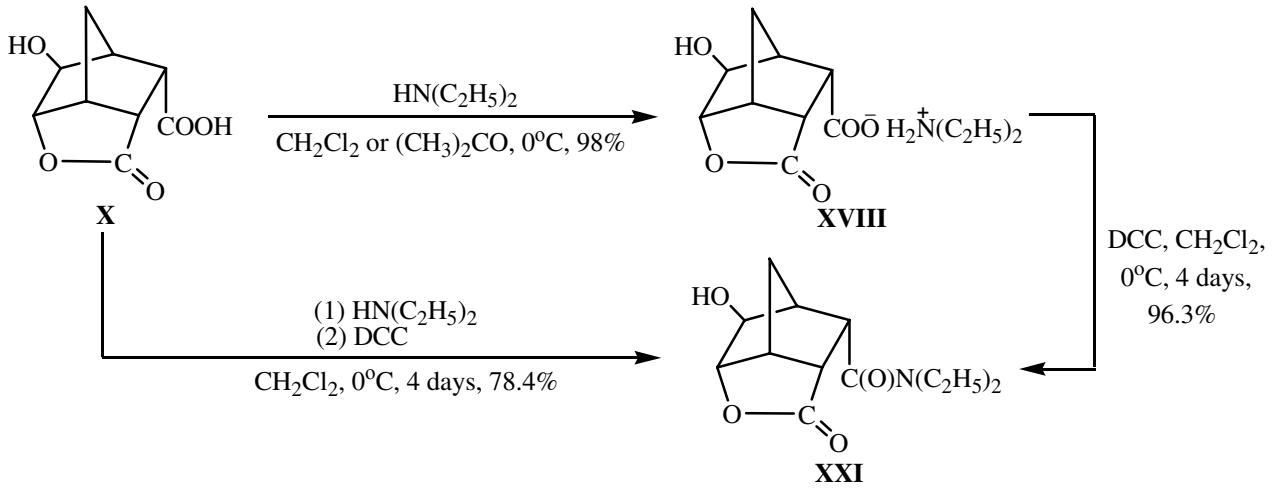
Analogously salt **XVI** was converted into the corresponding amidolactone **XXII** (Scheme 7). Inasmuch as bulky substituents at the nitrogen atom in this case considerably hampered the synthesis compared to the preparation of amidolactone **XXI** compound **XXII** was obtained under more stringent conditions and during longer time.

The IR spectrum of compound **XXI** contained absorption bands of two carbonyls: lactone (1800 cm^{-1}) and amide (1620 cm^{-1}) ones. The stretching vibrations of the hydroxy group give rise to a broad band in the region 3420 cm^{-1}. The spectrum contained also a strong

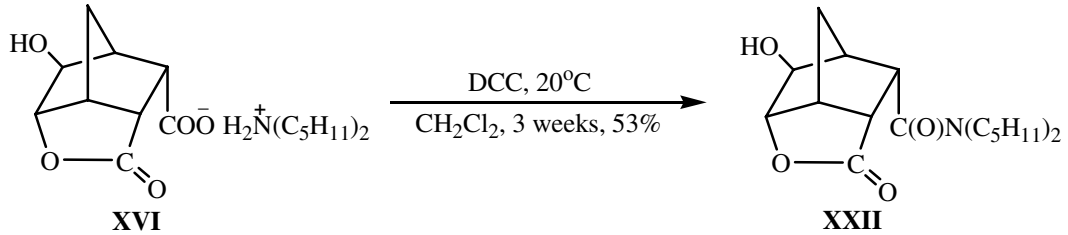


X, 51%

Scheme 6.



Scheme 7.



narrow peak in the region 1030 cm^{-1} assigned to the vibrations of the fragment C–O–C involved into the five-membered lactone ring [18].

The ^1H NMR spectra of compounds **XXI** and **XXII** contain all expected signals: *endo*-Proton H^2 and *exo*-proton H^3 give rise to peaks in the region 4.41–4.43 and 4.29 ppm respectively, a complex multiplet of H^7 proton is located at 3.17–3.19 ppm, the signals from the bridging protons H^{8s} and H^{8an} (1.96 and 1.52–1.53 ppm) suffer splitting due to the coupling with a geminal constant 10.4–10.5 Hz. Doublets of H^6 and H^9 protons appear at 2.65–2.68 and 3.02–3.15 ppm respectively and are additionally split by coupling with H^1 and H^7 protons; the value of the vicinal constant $^3J_{6,9}$ 10.2 Hz unambiguously con-firms their *exo*-orientation. A characteristic feature of the ^1H NMR spectrum of compound **XXI** is a pronounced nonequivalence of the protons of the ethyl groups in the carboxamide moiety: They appear as two two-proton quartets (3.12 and 3.32 ppm) and two three-proton triplets (0.96 and 1.13 ppm). In the ^1H NMR spectrum of com-pound **XXII** the nonequivalence of pentyl group protons is considerably less pronounced ($\Delta\delta$ 0.03 ppm) only for the methylene groups attached directly to the nitrogen of the amide.

The sum of data (the lack of the ammonium band in the IR spectra and of signals in the region 7.0–8.5 ppm of the ^1H NMR spectra, nonequivalence of ^1H nuclei in alkyl fragments) confirms that the structures of amido-lactones assigned to compounds **XXI** and **XXII** are valid.

EXPERIMENTAL

IR spectra were recorded on spectrometers UR-20 and Paragon 500 FT-IR (Perkin Elmer) from samples pelletized with potassium bromide. ^1H NMR spectra were registered on spectrometers Varian VXR at operating frequencies 200 and 300 MHz from solutions in deuterdimethyl sulfoxide and deuterochloroform, internal reference TMS. ^{13}C NMR spectra were registered on a spectrometer Gemini-400BB at operating frequency 100.57 MHz. Mass spectrum of salt **XVIII** was measured on Varian 1200L instrument at ionizing electrons energy 70 eV. The reaction progress was monitored and the purity of compounds synthesized was checked by TLC on Silufol UV-254 plates, eluents ethyl ether (A) and 2-propanol (B), development in iodine vapor. Elemental analysis was performed on Carlo Erba analyzer.

Crystals of salt **XVI** triclinic, $C_9H_9O_5^-\times C_{10}H_{24}N^+$, at 20°C *a* 11.946(2), *b* 13.814(3), *c* 14.197(2) Å, α 77.30(1), β 68.57(1), γ 72.54(2)°, *V* 2064.3(6) Å^3, M_r 709.92, *Z* 2, space group P^1, d_{calc} 1.142 g/cm^3, $\mu(MoK_\alpha)$ 0.082 mm^{-1}, *F*(000) 774. Unit cell parameters and intensities of 18665 reflections (7268 independent reflections, R_{int} 0.025) were measured on a diffractometer Xcalibur-3 (MoK_α radiation, CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 50°).

The structure was solved by the direct method using SHELXTL software [29]. The hydrogen atoms positions are calculated from geometric considerations, and those of hydrogen atoms at the nitrogen in cations **C** and **D** were revealed from the difference synthesis of the electron density. All hydrogen atoms positions were refined in the *rider* model with $U_{iso} = nU_{eq}$ (n = 1.5 for methyl and hydroxy groups and n = 1.2 for the other hydrogen atoms). The structure was refined by F^2 in full-matrix least-mean-square anisotropic approximation for nonhydrogen atoms till wR_2 0.225 for 7089 reflections (R_1 0.069 for 3433 reflections with $F > 4\sigma(F)$, *S* 0.923). The crystallographic data, atomic coordinates, and geometrical parameters of the structure are deposited in the Cambridge Structural Database (structure no. CCDC 299796).

The oxidation product of amide **IIg**, mixed crystals of lactonoacid **X** (50%) and salt **XVIII** (50%) monoclinic, $C_9H_{10}O_5$, $C_9H_9O_5^-C_4H_{12}N^+$, at –109°C *a* 13.172(3), *b* 19.679(4), *c* 10.123(2) Å, β 122.46(1)°, *V* 2214.1(8) Å^3, M_r 469.48, *Z* 4, space group *Cc*, d_{calc} 1.408 g/cm^3, $\mu(MoK_\alpha)$ 0.111 mm^{-1}, *F*(000) 1000. Unit cell parameters and intensities of 2038 independent reflections were measured on an automatic four-circle diffractometer Siemens P3/PC (MoK_α, , $\theta/2\theta$ scanning, $2\theta_{max}$ 50°).

The structure was solved by the direct method using SHELXTL software [29]. The hydrogen atoms positions are calculated from geometric considerations for the bicycloheptane framework and revealed from the difference synthesis of the electron density for the substituents at the framework fragment and for diethylammonium cation. All hydrogen atoms positions were refined in the *rider* model with $U_{iso} = nU_{eq}$ (n = 1.5 for methyl and hydroxy groups and n = 1.2 for the other hydrogen atoms). The structure was refined by F^2 in full-matrix least-mean-square anisotropic approximation for nonhydrogen atoms till wR_2 0.103 for 1973 reflections (R_1 0.044 for 1446 reflections with C $F > 4\sigma(F)$, *S* 1.058). The crystallographic data, atomic coordinates, and geometrical parameters of the structure are deposited in the Cambridge Structural Database (structure no. CCDC 299802).

Reaction of bicyclo[2.2.1]-hept-5-ene-*endo*,*endo*-2,3-dicarboxylic acid anhydride (I) with monoalkyl- and dialkylamines. To 3.28 g (0.02 mol) of endic anhydride (**I**) in 20–25 ml of anhydrous benzene was added at stirring 0.02 mol of an appropriate amine (ammonia and methylamine were used as 25% water solutions, dimethylamine, as 0.5 M benzene solution). The reaction mixture was stirred at room temperature till completion of the reaction (from 1 day to 3 weeks, TLC monitoring), the separated crystals were filtered off, washed on the filter with benzene, and dried in air. The products were additionally purified by recrystallization from benzene or 2-propanol. This procedure was applied to the synthesis of amido acids **IIa–IIj.**

***endo*-3-Carbamoylbicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IIa).** Yield 3.26 g (90%), mp 137–138°C [14]). R_f start (A), 0.80 (B). IR spectrum, cm^{-1}: 3450, 3362, 3080, 3050, 1700, 1670, 1540, 1395, 1338, 1252, 1200, 790, 700. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), d, ppm: 7.27 s (1H, NH), 6.58 s (1H, NH), 6.17 d.d (1H, H^6), 5.94 d.d (1H, H^5, $^3J_{5,6}$ 5.1, $^3J_{4,5} = {}^3J_{6,1}$ = 3.1 Hz), 3.16 d.d (1H, H^2), 3.14 d.d (1H, H^3), 3.05 m (1H, H^1), 3.02 m (1H, H^4), 1.20 d (1H, H^{7s}), 1.12 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.2 Hz). ^{13}C NMR spectrum (DMSO-d_6), d, ppm: 174.6 (C=O), 173.9 (C=O), 136.0 (C^6), 134.0 (C^5), 49.3 (C^2), 48.9 (C^3), 48.8 (C^7), 47.6 (C^1), 47.2 (C^4).

***endo*-3-(*N*-Methylcarbamoyl)bicyclo[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IIb).** Yield 3.51 g (90%), mp 155–157°C (155°C [7]), R_f 0.06 (A), 0.73 (B). IR spectrum, cm^{-1}: 3326, 3050, 1750, 1650, 1550, 1425, 1260, 714. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 7.64 br.s (1H, NH), 6.16 d.d (1H, H^6), 5.94 d.d (1H, H^5, $^3J_{5,6}$ 5.5, $^3J_{4,5} = {}^3J_{6,1}$ = 3.1 Hz), 3.13 d.d (1H, H^2), 3.06 d.d (1H, H^3, $^3J_{2,3}$ 10.2, $^3J_{1,2} = {}^3J_{3,4}$ = 3.1 Hz), 3.01 m (1H, H^1), 2.92 m (1H, H^4), 2.48 s (3H, CH_3), 1.26 d (1H, H^{7s}), 1.20 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 173.4 (C=O), 171.5 (C=O), 134.8 (C^6), 133.7 (C^5), 48.3 (C^2), 48.2 (C^3), 48.1 (C^7), 46.6 (C^1), 45.3 (C^4), 25.5 (CH_3).

***endo*-3-(*N*-Benzylcarbamoyl)bicyclo[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IIc).** Yield 4.88 g (90%), mp 118–119.5°C (118–120°C [15]), R_f 0.49 (A), 0.78 (B). IR spectrum, cm^{-1}: 3280, 3030, 1770, 1650, 1514, 1486, 1267, 1207, 745. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 7.26 m (5H$_{arom}$), 6.69 br.s (1H, NH), 6.32 d.d (1H, H^6), 5.98 d.d (1H, H^5, $^3J_{5,6}$ 5.2, $^3J_{4,5} = {}^3J_{6,1}$ = 3.0 Hz), 4.26 d (1H, NCH), 4.06 d (1H, NCH, $^2J_{H,H}$ 14.3, $^2J_{HNH}$ 5.5 Hz), 3.16 d.d (1H, H^2), 3.11 d.d (1H, H^3, $^3J_{2,3}$ 10.0, $^3J_{1,2} = {}^3J_{3,4}$ = 3.0 Hz), 3.01 m (1H, H^1), 2.96 m (1H, H^4), 1.35 d (1H, H^{7s}), 1.20 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.5 Hz).

***endo*-3-(*N,N*-Dimethylcarbamoyl)bicyclo-[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IId).** Yield 3.09 g (74%), mp 150–151°C [15], R_f 0.83 (A). IR spectrum, cm^{-1}: 3455, 3020, 1750, 1645, 1530, 1340, 1200, 718. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 11.74 s (1H, COOH), 6.22 d.d (1H, H^6), 5.93 d.d (1H, H^5, $^3J_{5,6}$ 5.3, $^3J_{4,5} = {}^3J_{6,1}$ = 2.8 Hz), 3.38 d.d (1H, H^2), 3.29 d.d (1H, H^3, $^3J_{2,3}$ 10.1, $^3J_{1,2} = {}^3J_{3,4}$ = 3.0 Hz), 3.03 m (1H, H^1), 2.92 m (1H, H^4), 2.92 C (3H, CH_3), 2.69 s (3H, CH_3), 1.34 d (1H, H^{7s}), 1.22 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.1 Hz).

***endo*-3-(N-Methyl-*N*-benzylcarbamoyl)bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IIe).** Yield 4.85 g (85%), mp 135.5–136°C, R_f 0.61 (A), 0.67 (B). IR spectrum, cm^{-1}: 3460, 3010, 1750, 1625, 1505, 1460, 1425, 1345, 1265, 1195, 705. Found, %: C 71.51; H 6.71; N 4.99. $C_{17}H_{19}NO_3$. Calculated, %: C 71.58; H 6.67; N 4.91.

***endo*-3-(*N,N*-Dibenzylcarbamoyl)bicyclo-[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IIf).** Yield 2.89 g (40%), mp 139.5–140°C, R_f 0.13 (A), 0.76 (B). IR spectrum, cm^{-1}: 3420, 3010, 1710, 1625, 1540, 1495, 1255, 712. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 7.42–7.29 (10H$_{arom}$), 6.09 m (2H, H^5, H^6), 3.85 s (4H, 2CH_2), 3.09 m (2H, H^2, H^3), 3.05 m (2H, H^1, H^4), 1.28 d (1H, H^{7s}), 1.20 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.2 Hz). Found, %: C 76.49; H 6.41; N 3.86. $C_{23}H_{23}NO_3$. Calculated, %: C 76.45; H 6.37; N 3.88.

***endo*-3-(*N,N*-Diethylcarbamoyl)bicyclo[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IIg).** Yield 4.08 g (86%), mp 102–104°C, R_f 0.31 (A), 0.72 (B). IR spectrum, cm^{-1}: 3460, 3010, 1745, 1625, 1480, 1405, 1280, 1190, 730. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 11.60 s (1H, COOH), 6.16 d.d (1H, H^6), 5.98 d.d (1H, H^5, $^3J_{5,6}$ 5.3, $^3J_{4,5} = {}^3J_{6,1}$ = 2.7 Hz), 3.38 q (2H, CH_2), 3.11 q (2H, CH_2), 3.01 d.d (1H, H^2), 2.96 d.d (1H, H^3), 2.90 m (1H, H^1), 2.86 m (1H, H^4), 1.34 d (1H, H^{7s}), 1.20 d (1H, H^{7an}, $^2J_{7s,7an}$ 8.1 Hz), 1.10 t (3H, CH_3), 0.92 t (3H, CH_3). Found, %: C 65.89; H 7.99; N 5.79. $C_{13}H_{19}NO_3$. Calculated, %: C 65.82; H 8.02; N 5.91.

***endo*-3-(*N,N*-Dipropylcarbamoyl)bicyclo-[2.2.1]-hept-5-ene-*endo*-2-carboxylic acid (IIh).** Yield 4.29 g (81%), mp 111–112.5°C, R_f start (A), 0.57 (B). IR spectrum, cm^{-1}: 3450, 3010, 1742, 1582, 1482, 1420, 1350, 1312, 735, 710. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 6.05 m (2H, H^5, H^6), 3.15 m (2H, H^2, H^3), 3.00 m (2H, H^1, H^4), 2.70 t (4H, 2CH_2), 1.58 m

(4H, $2CH_2$), 1.25 m (2H, H^{7s}, H^{7an}), 0.95 t (6H, $2CH_3$). Found, %: C 67.98; H 8.60; N 5.36. $C_{15}H_{23}NO_3$. Calculated, %: C 67.92; H 8.68; N 5.28.

***endo*-3-(*N,N*-Diisopropylcarbamoyl)bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IIi).** Yield 2.12 g (40%), mp 137–138.5°C, R_f 0.19 (B). IR spectrum, cm^{-1}: 3460, 3050, 1690, 1625, 1600, 1490, 1400, 1340, 1220, 1165, 740, 725. Found, %: C 67.86; H 8.75; N 5.25. $C_{15}H_{23}NO_3$. Calculated, %: C 67.92; H 8.68; N 5.28.

***endo*-3-(*N,N*-Dipentylcarbamoyl)bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (IIj).** Yield 4.56 g (71%), mp 135–137°C, R_f Ctapt (A), 0.63 (B). IR spectrum, cm^{-1}: 3126, 3068, 1728, 1564, 1464, 1422, 1378, 1288, 1202, 720. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 6.04 m (2H, H^6, H^5), 3.09 m (2H, H^2, H^3), 2.95 m (2H, H^1, H^4), 2.81 t (4H, $2CH_2$), 1.52 m (4H, $2CH_2$), 1.27 m (8H, $4CH_2$), 1.21 d (1H, H^{7s}), 1.11 d (1H, H^{7an}, $^2J_{7s,7an}$ 9.1 Hz), 0.85 t (6H, $2CH_3$). Found, %: C 70.99; H 9.71; N 4.28. $C_{19}H_{31}NO_3$. Calculated, %: C 71.03; H 9.66; N 4.36.

***exo*-2-Hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]-nonane-*endo*-9-carboxylic acid (X).** *a*. The compound was obtained by procedure used in oxidation of amido acids (see further) from anhydride **I**, amide **IIb** and **IId**, or acid **III**. Yields 0.33 g (83%), 0.28 g (70%), 0.34 g (85%), and 0.38 g (96%) respectively, mp 200–202°C (from acetone) (202–203°C [25]), R_f 0.10 (A), 0.58 (B). IR spectrum, cm^{-1}: 3400, 1766, 1726, 1412, 1324, 1198, 1060, 1036, 1006. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 12.56 br.s (1H, COOH), 5.24 br.s (1H, OH), 4.31 d (1H, H^3, $^3J_{3,7}$ 5.0 Hz), 4.01 s (1H, H^2), 3.19 m (1H, H^7), 3.04 d.d (1H, H^9, $^3J_{6,9}$ 10.8, $^3J_{9,1}$ 3.8 Hz), 2.66 d.d (1H, H^6, $^3J_{6,7}$ 4.5 Hz), 2.41 br.s (1H, H^1), 1.95 d (1H, H^{8s}), 1.50 d (1H, H^{8a}, $^2J_{8s,8a}$ 10.7 Hz).

b. To a solution of 0.61 g (2 mmol) of salt **XVII** in 15 ml of water 0.33 ml (2 mmol) of 20% solution of hydrochloric acid was added, and the mixture obtained was evaporated in a vacuum. The solid residue was treated with hot acetone, and the benzylamine hydrochloride was filtered off. On cooling the acetone filtrate crystals of compound **X** precipitated. Yield 0.20 g (51%).

Oxidation of amido acids of norbornene series with performic acid *in situ*. To 2 mmol of an appropriate amido acid **IIa–IIj** in 5–8 ml of 98% formic acid was added dropwise while stirring at 0°C 0.23 ml (4 mmol) of 50% water solution of hydrogen peroxide, and the stirring at this temperature was continued till the completion of the reaction (TLC monitoring). The formic acid was removed in a vacuum, ethyl ether was added to the oily residue, and after prolong at grinding in the cold the formed crystals were filtered off and dried. This procedure was used in preparation of compounds **XI–XVIII**.

Ammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XI). Yield 0.37 g (86%), mp 155–158°C, R_f 0.06 (B). IR spectrum, cm^{-1}: 3215, 3060, 1780, 1725, 1595, 1425, 1360, 1175, 1025, 790. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 8.36 br.s (4H, H_4N^+), 6.19 br.s (1H, OH), 4.26 d (1H, H^3, $^3J_{3,7}$ 5.6 Hz), 4.06 s (1H, H^2), 3.13 m (1H, H^7), 2.90 d.d (1H, H^9, $^3J_{9,1}$ 3.7, $^3J_{6,9}$ 10.5 Hz), 2.54 d.d (1H, H^6, $^3J_{6,7}$ 5.0 Hz), 2.36 br.s (1H, H^1), 1.90 d (1H, H^{8s}), 1.44 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.5 Hz). Found, %: C 50.30; H 6.02; N 6.59. $C_9H_{13}NO_5$. Calculated, %: C 50.23; H 6.05; N 6.51.

***N*-Methyl-*N*-benzylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XII).** Yield 0.50 g (79%), mp 164–166°C, R_f 0.13 (B). IR spectrum, cm^{-1}: 3400, 2550, 1790, 1735, 1675, 1600, 1410, 1365, 1220, 1175, 1030, 765. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 8.23 br.s (2H, H_2N^+), 7.46–7.21 ($5H_{arom}$), 6.78 br.s (1H, OH), 4.44 s (2H, CH_2), 4.31 d (1H, H^3, $^3J_{3,7}$ 5.1 Hz), 4.05 C (1H, H^2), 3.18 m (1H, H^7), 3.02 d.d (1H, H^9, $^3J_{9,1}$ 3.0, $^3J_{6,9}$ 10.5 Hz), 2.64 d.d (1H, H^6, $^3J_{6,7}$ 4.5 Hz), 2.63 s (3H, CH_3), 2.42 br.s (1H, H^1), 1.96 d (1H, H^{8s}), 1.50 d (1H, H^{8an}, $^2J_{8s,8an}$ 11.0 Hz). Found, %: C 63.88; H 6.61; N 4.40. $C_{17}H_{21}NO_5$. Calculated, %: C 63.95; H 6.58; N 4.39.

Dibenzylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XIII). Yield 0.66 g (83%), mp 101–104°C, R_f 0.38 (B). IR spectrum, cm^{-1}: 3415, 2640, 1780, 1735, 1600, 1360, 1220, 1175, 1030, 765. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 8.30 br.s (2H, H_2N^+), 7.43–7.30 ($10H_{arom}$), 4.35 br.s (1H, OH), 4.30 d (1H, H^3, $^3J_{3,7}$ 4.8 Hz), 4.07 s (1H, H^2), 3.89 s (4H, $2CH_2$), 3.16 m (1H, H^7), 2.99 d.d (1H, H^9, $^3J_{9,1}$ 2.4, $^3J_{6,9}$ 10.5 Hz), 2.62 d.d (1H, H^6, $^3J_{6,7}$ 4.5 Hz), 2.41 br.s (1H, H^1), 1.94 d (1H, H^{8s}), 1.48 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.5 Hz). Found, %: C 69.91; H 6.40; N 3.49. $C_{23}H_{25}NO_5$. Calculated, %: C 69.87; H 6.33; N 3.54.

Dipropylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XIV). Yield 0.48 g (81%), oily substance, R_f 0.25 (B). IR spectrum, cm^{-1}: 3400, 2560, 1785, 1600, 1355, 1210, 1170, 1030, 770. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 8.38 br.s (2H, H_2N^+), 4.22 d (1H, H^3,

$^3J_{3,7}$ 5.6 Hz), 4.09 s (1H, H^2), 3.08 m (1H, H^7), 2.82 d.d (1H, H^9, $^3J_{9,1}$ 3.0, $^3J_{6,9}$ 10.8 Hz), 2.73 t (4H, $2CH_2$), 2.48 d.d (1H, H^6, $^3J_{6,7}$ 4.8 Hz), 2.33 br.s (1H, H^1), 1.88 d (1H, H^{8s}), 1.67–1.48 m (4H, $2CH_2$), 1.40 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.4 Hz), 0.86 t (6H, $2CH_3$). Found, %: C 60.23; H 8.40; N 4.60. $C_{15}H_{25}NO_5$. Calculated, %: C 60.20; H 8.36; N 4.68.

Diisopropylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XV). Yield 0.40 g (67%), oily substance, R_f 0.12 (B). IR spectrum, cm^{-1}: 3400, 2495, 1785, 1720, 1600, 1360, 1220, 1180, 1030, 770. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 8.34 br.s (2H, H_2N^+), 4.86 br.s (1H, OH), 4.27 d (1H, H^3, $^3J_{3,7}$ 5.4 Hz), 4.03 s (1H, H^2), 3.52 d.d (1H, H^9, $^3J_{9,1}$ 4.2, $^3J_{6,9}$ 10.6 Hz), 3.14 m (1H, H^7), 3.00 m (2H, 2CH), 2.57 d.d (1H, H^6, $^3J_{6,7}$ 4.5 Hz), 2.37 br.s (1H, H^1), 1.98 d (1H, H^{8s}), 1.55 d (1H, H^{8an}, $^2J_{8s,8an}$ 11.4 Hz), 1.20 d (12H, $4CH_3$). Found, %: C 60.16; H 8.41; N 4.70. $C_{15}H_{25}NO_5$. Calculated, %: C 60.20; H 8.36; N 4.68.

Dipentylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XVI). Yield 0.46 g (65%), mp 99–101°C, R_f 0.44 (B). IR spectrum, cm^{-1}: 3398, 2550, 1774, 1724, 1586, 1410, 1350, 1200, 1168, 1016, 763. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 7.35 br.s (2H, H_2N^+), 4.24 d (1H, H^3, $^3J_{3,7}$ 5.6 Hz), 4.10 s (1H, H^2), 3.10 m (1H, H^7), 2.87 d.d (1H, H^9, $^3J_{9,1}$ 3.2, $^3J_{6,9}$ 10.6 Hz), 2.74 t (4H, $2CH_2$), 2.51 d.d (1H, H^6, $^3J_{6,7}$ 3.7 Hz), 2.35 br.s (1H, H^1), 1.90 d (1H, H^{8s}), 1.63–1.48 m (4H, $2CH_2$), 1.43 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.8 Hz), 1.29–1.22 m (8H, $4CH_2$), 0.86 t (6H, $2CH_3$). Found, %: C 64.16; H 9.31; N 4.00. $C_{19}H_{33}NO_5$. Calculated, %: C 64.23; H 9.30; N 3.94.

Benzylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XVII). *a*. Yield 0.46 g (75%), mp 139–140.5°C, R_f 0.20 (B). IR spectrum, cm^{-1}: 3212, 3014, 1766, 1724, 1604, 1368, 1180, 1014, 788. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 8.34 br.s (3H, H_3N^+), 7.47–7.27 ($5H_{arom}$), 5.34 br.s (1H, OH), 4.28 d (1H, H^3, $^3J_{3,7}$ 5.1 Hz), 4.06 s (1H, H^2), 4.00 s (2H, CH_2), 3.14 m (1H, H^7), 2.95 d.d (1H, H^9, $^3J_{9,1}$ 3.2, $^3J_{6,9}$ 10.5 Hz), 2.59 d.d (1H, H^6, $^3J_{6,7}$ 5.1 Hz), 2.39 br.s (1H, H^1), 1.93 d (1H, H^{8s}), 1.46 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.8 Hz). Found, %: C 62.88; H 6.29; N 4.63. $C_{16}H_{19}NO_5$. Calculated, %: C 62.95; H 6.23; N 4.59.

b. To a solution of 0.54 g (2 mmol) of amido acid **IIc** in 8 ml of 98% formic acid was added dropwise while stirring at 0°C 0.45 ml (8 mmol) of 50% water solution of hydrogen peroxide, and the stirring at this temperature was continued till the completion of the reaction (TLC monitoring). The formic acid was removed in a vacuum, ethyl ether was added to the oily residue, and after prolonged grinding in the cold the formed crystals were filtered off and dried. Yield 0.45 g (74%).

c. To 0.54 g (2 mmol) of amido acid **IIc** dissolved in a mixture of dichloromethane and acetonitrile (3:1 v/v) was added dropwise while stirring at 0°C 0.15 ml (4 mmol) of 98% formic acid and 0.23 ml (4 mmol) of 50% water solution of hydrogen peroxide, and the stirring at this temperature was continued till the completion of the reaction (TLC monitoring). The volatile substances were removed in a vacuum. After a usual workup we obtained the target product in 0.43 g (71%) yield.

d. To 0.54 g (2 mmol) of amido acid **IIc** in 8 ml of glacial acetic acid was added dropwise while stirring at room temperature (17°C) 0.23 ml (4 mmol) of 50% water solution of hydrogen peroxide, and the stirring at this temperature was continued till the completion of the reaction (TLC monitoring). The acetic acid was removed in a vacuum. After a usual workup we obtained the target product in 0.43 g (70%) yield.

Mixture of diethylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XVIII) (50%) with *exo*-2-hydroxy-5-oxo-4-oxatricyclo[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylic acid (X) (50%). Yield 0.35 g (74%), R_f 0.12 and 0.58 (B). IR spectrum, cm^{-1}: 3300, 3185, 2650, 1785, 1725, 1585, 1360, 1240, 1170, 1025, 765. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 7.50 br.s (2H, H_2N^+), 6.30 br.s (2H, OH), 4.23 d (2H, H^3, $^3J_{3,7}$ 5.1 Hz), 4.14 s (2H, H^2), 3.10 m (2H, H^7), 2.81 d.d (2H, H^9, $^3J_{6,9}$ 10.8 Hz), 2.81 q (4H, $2CH_2$), 2.49 d.d (2H, H^6, $^3J_{6,7}$ 3.9 Hz), 2.34 br.s (2H, H^1), 1.89 d (2H, H^{8s}), 1.41 d (2H, H^{8an}, $^2J_{8s,8an}$ 10.7 Hz), 1.14 t (6H, $2CH_3$). ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 8.47 br.s (2H, H_2N^+), 4.45 d (2H, H^3, $^3J_{3,7}$ 4.8 Hz), 4.26 s (2H, H^2), 4.13 br.s (2H, OH), 3.22 m (2H, H^7), 2.97 d.d (2H, H^9, $^3J_{6,9}$ 10.1 Hz), 2.97 q (4H, $2CH_2$), 2.63 d.d (2H, H^6, $^3J_{6,7}$ 4.1 Hz), 2.63 br.s (2H, H^1), 2.12 d (2H, H^{8s}), 1.56 d (2H, H^{8an}, $^2J_{8s,8an}$ 11.0 Hz), 1.31 t (6H, $2CH_3$).

Diethylammonium *exo*-2-hydroxy-5-oxo-4-oxatricyclo-[4.2.1.0^{3,7}]nonane-*endo*-9-carboxylate (XVIII). *a*. To 0.47 g (2 mmol) of amido acid **IIg** in 8 ml of glacial acetic acid was added dropwise at room temperature (20°C) while stirring 0.23 ml (4 mmol) of 50% water solution of hydrogen peroxide, and the stirring at this temperature was continued till the completion of

the reaction (TLC monitoring). The acetic acid was removed in a vacuum. After a usual workup we obtained the target product in 0.34 g (63%) yield, mp 147–150°C, R_f 0.12 (B). IR spectrum, cm^{-1}: 3390, 2530, 1780, 1595, 1415, 1360, 1220, 1180, 1030, 775. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 7.50 br.s (2H, H_2N^+), 6.30 br.s (1H, OH), 4.23 d (1H, H^3, $^3J_{3,7}$ 5.1 Hz), 4.15 s (1H, H^2), 3.10 m (1H, H^7), 2.81 d.d (1H, H^9, $^3J_{6,9}$ 10.8 Hz), 2.81 q (4H, $2CH_2$), 2.49 d.d (1H, H^6, $^3J_{6,7}$ 3.9 Hz), 2.34 br.s (1H, H^1), 1.89 d (1H, H^{8s}), 1.41 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.7 Hz), 1.14 t (6H, $2CH_3$).

b. To 0.47 g (2 mmol) of amido acid **IIg** in 10 ml of chloroform was added 0.34 g (4 mmol) of sodium hydrogen carbonate, then dropwise was added at stirring 0.38 ml (4 mmol) of freshly distilled acetic anhydride and 0.23 ml (4 mmol) of 50% water solution of hydrogen peroxide, and the stirring at room temperature (20°C) was continued till the completion of the reaction (TLC monitoring). The volatile substances were removed in a vacuum. After a usual workup we obtained the target product in 0.35 g (65%) yield.

c. A mixture of 0.47 g (2 mmol) of amido acid **IIg**, 1.16 g (4 mmol) of 54% *m*-chloroperbenzoic acid in 15 ml of anhydrous dichloromethane was stirred at room temperature for 48 h till the completion of the reaction (TLC monitoring). The formed *m*-chlorobenzoic acid was neutralized with a saturated water solution of sodium carbonate. The water layer was separated, evaporated in air at room temperature, the solid residue was treated with a solvent mixture chloroform–acetonitrile–2-propanol, 1:1:1 by volume, the solution was filtered, and the solvent was removed in a vacuum. After a usual workup we obtained the target product in 0.17 g (31%) yield.

d. A mixture of 0.47 g (2 mmol) of amido acid **IIg**, 0.06 g (1 mmol) of urea, 1.12 g (4 mmol) of freshly prepared 65% monoperoxyphthalic acid in 20 ml of ethyl acetate was stirred at room temperature for 48 h till the completion of the reaction (TLC monitoring). The formed phthalic acid was neutralized with a saturated water solution of sodium carbonate. The water layer was separated, evaporated in air at room temperature, the solid residue was treated with a solvent mixture chloroform–acetonitrile–2-propanol, 1:1:1 by volume, the solution was filtered, and the solvent was removed in a vacuum. After a usual workup we obtained the target product in 0.27 g (49%) yield.

***N,N*-Diethyl-*exo*-2-hydroxy-5-oxo-4-oxatricyclo[4.2.1.0^{3,7}]nonane-*endo*-9-carboxamide (XXI).** *a*. To a mixture of 0.40 g (2 mmol) of lactonoacid **X** and 10 ml of anhydrous dichloromethane at 0°C was added while stirring 0.21 ml (2 mmol) of freshly distilled diethylamine and a solution of 0.41 g (2 mmol) of dicyclohexylcarbodiimide in 5 ml of anhydrous dichloromethane. After stirring for 4 days the precipitate of dicyclohexylurea was filtered off. The filtrate was evaporated in a vacuum, the residue was ground under a layer of ethyl ether, the formed crystals were filtered off, washed with ether, and recrystallized from 2-propanol. Yield 0.39 g (78%), mp 161–163.5°C, R_f 0.45 (B). IR spectrum, cm^{-1}: 3420, 1800, 1620, 1460, 1150, 1085, 1030. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 5.07 s (1H, OH), 4.29 d (1H, H^3, $^3J_{3,7}$ 5.1 Hz), 4.43 s (1H, H^2), 3.32 q (2H, CH_2), 3.19 m (1H, H^7), 3.15 d.d (1H, H^9, $^3J_{9,1}$ 3.9, $^3J_{6,9}$ 10.2 Hz), 3.12 q (2H, CH_2), 2.68 d.d (1H, H^6, $^3J_{6,7}$ 4.8 Hz), 2.29 br.s (1H, H^1), 1.96 d (1H, H^{8s}), 1.52 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.5 Hz), 1.13 t (3H, CH_3), 0.96 t (3H, CH_3). Found, %: C 61.71; H 7.48; N 5.49. $C_{13}H_{19}NO_4$. Calculated, %: C 61.66; H 7.51; N 5.53.

b. To a mixture of 0.40 g (2 mmol) of lactonoacid **X** in 5 ml of anhydrous acetone was added 0.21 ml (2 mmol) of freshly distilled diethylamine. The mixture was stirred at room temperature for 24 h. The reaction product was filtered off, washed with a little anhydrous acetone, and dried. To the dispersion of 0.54 g (2 mmol) of obtained salt **XV** in 10 ml of anhydrous dichloromethane was added at 0°C while stirring a solution of 0.41 g (2 mmol) of dicyclohexylcarbodiimide in 5 ml of anhydrous dichloromethane. After stirring for 4 days the precipitate of dicyclohexylurea was filtered off. The filtrate was evaporated in a vacuum to dryness, the residue was ground under a layer of ethyl ether, the formed crystals were filtered off, washed with ether, and recrystallized from 2-propanol. Yield 0.49 g (96%).

***N,N*-Dipentyl-*exo*-2-hydroxy-5-oxo-4-oxatricyclo[4.2.1.0^{3,7}]nonane-*endo*-9-carboxamide (XXII).** To a solution of 0.71 g (2 mmol) of salt **XVI** in 15 ml of anhydrous dichloromethane was added at room temperature while stirring a solution of 0.41 g (2 mmol) of dicyclohexylcarbodiimide in 5 ml of anhydrous dichloromethane. After stirring for 4 days the precipitate of dicyclohexylurea was filtered off. The filtrate was evaporated in a vacuum to dryness, the residue was ground under a layer of ethyl ether, the formed crystals were filtered off, washed with ether, and dried. The evaporation of the ether filtrate to 1/3 of its volume provided a second portion of the reaction product. The combined product was recrystallized from 2-propanol.

Yield 0.36 g (53%), mp 110–112°C, R_f 0.82 (B). ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm: 5.07 d (1H, OH, $^3J_{OH,2}$ 3.6 Hz), 4.41 d (1H, H^2), 4.29 d (1H, H^3, $^3J_{3,7}$ 5.1 Hz), 3.19 t (2H, CH_2), 3.17 m (1H, H^7), 3.16 t (2H, CH_2), 3.02 d.d (1H, H^9, $^3J_{9,1}$ 3.3, $^3J_{6,9}$ 10.2 Hz), 2.65 d.d (1H, H^6, $^3J_{6,7}$ 5.0 Hz), 2.28 br.s (1H, H^1), 1.96 d (1H, H^{8s}), 1.53 d (1H, H^{8an}, $^2J_{8s,8an}$ 10.4 Hz), 1.28 m (12H, $6CH_2$), 0.87 t (6H, $2CH_3$). Found, %: C 67.69; H 9.16; N 4.12. $C_{19}H_{31}NO_4$. Calculated, %: C 67.66; H 9.20; N 4.15.

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