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Esters of Substituted 2,3,7-Triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids and 1,2,7-Triazaspiro[4.4]non-2-ene-3-carboxylic acids in Alkylation and Acylation

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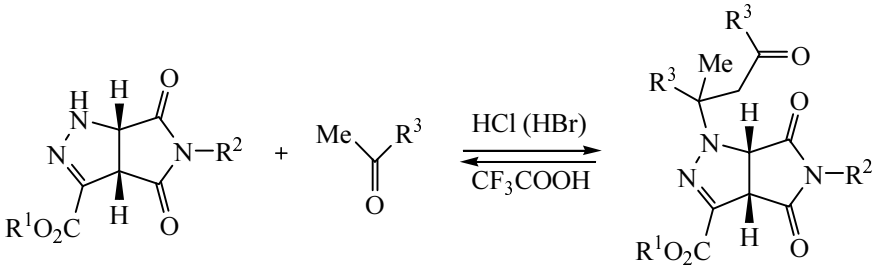
Abstract—Esters of substituted 2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids react with acetone in the presence of hydrogen chloride (bromide) affording esters of substituted 2-(1,1-dimethyl-3-oxobutyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids. Reactions of esters of substituted 2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylic acids with 1-adamantanol in trifluoroacetic acid resulted in esters of substituted 2-(1-adamantyl)-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylic acids.

Alkylation and acylation reactions of monocyclic pyrazolines are well documented [1–3], whereas these processes are virtually unknown for pyrazolines obtained by 1,3-dipolar cycloaddition of aliphatic diazo compounds to an activated multiple bond. Reaction of benzyl bromide with 1-pyrazoline prepared from bicyclo[2.2.1]heptane and diazocyclopropane occurred as a formal 1,5-addition to the azacycloprpane system affording 1-benzyl-2-pyrazoline [4].

We investigated alkylation of bi- and spirocyclic 2-pyrazolines by aliphatic ketones and adamantanol under acid catalysis, and also acylation reactions. Reactions of esters of substituted 6,8-dioxo-2,3,7-triazabicyclo[3.3.0]-oct-3-ene-4-carboxylic acids **Ia–Ik** with acetone in the presence of gaseous HCl or HBr gave rise to esters of substituted 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids **IIa–IIk** in 72–94% yields (Scheme 1). In the IR spectra of these compounds an absorption band was observed in the region 1720 cm^{-1} (C=O). The UV spectra of compounds **IId** and **IIe** contained an absorption maximum at 312–315 nm characteristic of compounds possessing an azomethine group in conjugation with an ester group. In the ^1H NMR spectra of compounds **IIa–IIk** doublets appear belonging to protons attached to C^1 and C^5 in the region 5.5 and 4.8 ppm (J 11 Hz) respectively, and

Scheme 1.



Ia–In **IIa–IIk, IIIa–IIIc, IV, V, VI**

I, R^1 = Et, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$CH_3OC_6H_4$ (**c**), *cyclo*-C_6H_{11} (**d**), 3,4-$(CH_3)_2C_6H_3$ (**e**), 4-FC_6H_4 (**f**); R^1 = Me, R^3 = 4-ClC_6H_4 (**g**), 4-$CH_3C_6H_4$ (**h**), 4-BrC_6H_4 (**i**), 3,5-$Cl_2C_6H_3$ (**j**), 4-$MeOC_6H_4$ (**k**), 4-$EtOC_6H_4$ (l), Ph (**m**), 3-$MeOC_6H_4$ (**n**); **II**, R^1 = Et, R^3 = Me, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$CH_3OC_6H_4$ (**c**), *cyclo*-C_6H_{11} (**d**), 3,4-$(CH_3)_2C_6H_3$ (**e**), 4-FC_6H_4 (**f**); $R^1 = R^3$ = Me, R^2 = 4-ClC_6H_4 (**g**), 4-$CH_3C_6H_4$ (**h**), 4-BrC_6H_4 (**i**), 3,5-$Cl_2C_6H_3$ (**j**), 4-$MeOC_6H_4$ (**k**); **III**, R^1 = Me, R^3 = Et, R^2 = 4-$CH_3C_6H_4$ (**a**), 4-$EtOC_6H_4$ (**b**), 4-$MeOC_6H_4$ (**c**); **IV**, R^1 = Me, R^2 = 4-$EtOC_6H_4$, R^3 = Pr; **V**, R^1 = Me, R^2 = Ph, R^3 = Bu; **VI**, R^1 = Me, R^2 = 4-$CH_3C_6H_4$, R^3 = C_7H_{15}.

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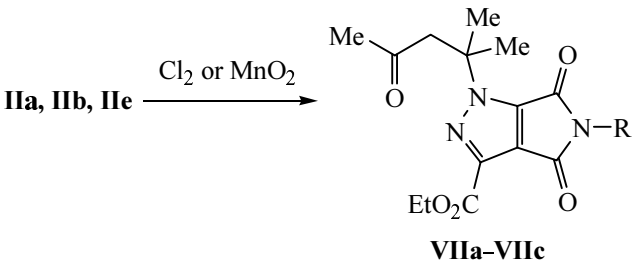
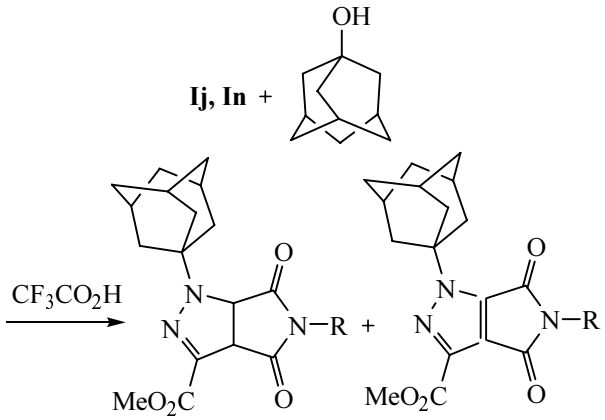
Scheme 2.



VIIa–VIIc

R = Ph (**a**), 4-ClC_6H_4 (**b**), 3,4-$(CH_3)_2C_6H_3$ (**c**).

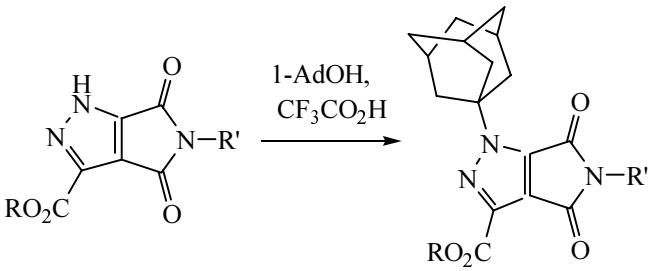
Scheme 3.



VIIIa, VIIIb **IX**

VIII, R = 3-$MeOC_6H_4$ (**a**), 3,5-$Cl_2C_6H_3$ (**b**); **IX**, R = 3,5-$Cl_2C_6H_3$.

Scheme 4.



Xa–**Xj** **XIa**–**XIj**

X, XI, R = Me, R' = Ph (**a**), 4-EtC_6H_4 (**b**), 4-FC_6H_4 (**c**); R = Et, R' = 3-Me-4-BrC_6H_3 (**d**), *cyclo*-C_6H_{11} (**e**), Ph (**f**), 4-MeC_6H_4 (**g**), 4-ClC_6H_4 (**h**), 4-BrC_6H_4 (**i**), 4-EtC_6H_4 (**j**).

belonging to protons of the methylene group of the alkyl substituent in the region 2.9 and 3.1 ppm with a coupling constant 17 Hz. The signals of the geminal methyl groups are observed in the region 1.5 and 1.6 ppm. On keeping compounds **IIa, IIb** for 12 h in trifluoroacetic acid at room temperature dealkylation occurred resulting in nearly quantitative recovery of the initial pyrazolines.

On increasing the hydrocarbon chain in the ketone the yield of alkylation products significantly decreased. Reactions of pyrazolines **Ih, Ik,** and **Il** with 2-butanone in the presence of gaseous HBr gave rise to mixtures of products. From these mixtures by column chromatography esters were isolated of diastereomeric 7-aryl-6,8-dioxo-2-(1-methyl-1-ethyl-3-oxopentyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids **IIIa–IIIc** in up to 27% yield. In reactions with 2-pentanone, 2-hexanone, and 2-nonanone adducts **IV–VI** formed in 21, 15,and 7% yield respectively.

The structure and composition of compounds **IIIa–IIIc** were confirmed by spectral data and elemental analyses. Esters **IIIa–IIIc, IV–VI** according to ^{1}H NMR spectra exist as two diastereomers in a ratio 2:1. The signals of protons at bridgehead carbons in the prevailing diastereomer appear downfield (4.8 and 5.6 ppm, *J* 12 Hz) compared to those of the minor isomer (4.7 and 5.4 ppm, *J* 11 Hz). In the spectrum two sets of doublet signals are also observed belonging to an isolated methylene group of the alkyl substituent: at 2.7 and 3.1 ppm (*J* 17 Hz) for the major isomer, and at 2.9 and 3.0 ppm (*J* 17 Hz) for the minor isomer. We failed to separate the diastereomers. It should be remarked that the attempt to prepare by this procedure N-alkylated analogs of spirocyclic pyrazolines **XII** was unsuccessful: Only the initial pyrazolines were recovered from the reaction mixture.

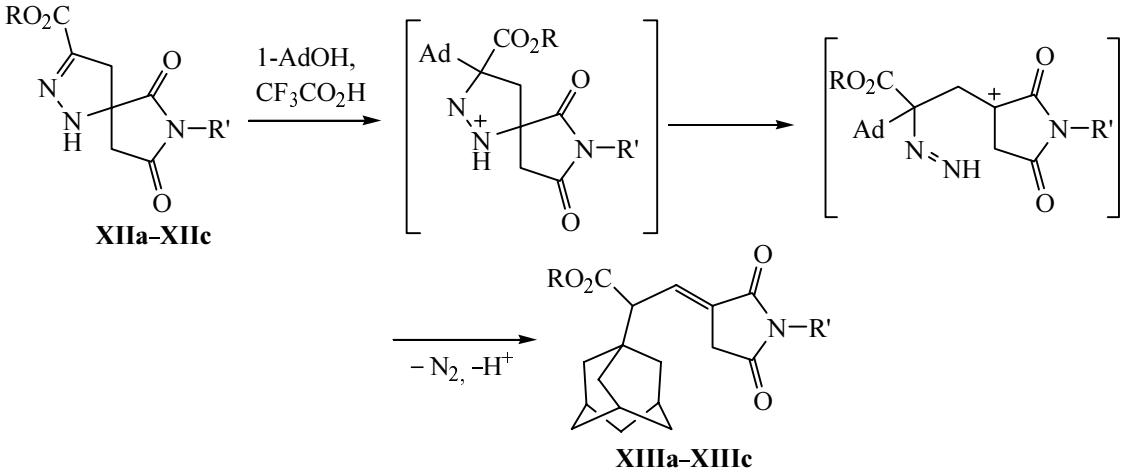
Pyrazolines **IIa, IIb,** and **IIe** were converted into the corresponding pyrazoles **VIIa–VIIc** in moderate yields (40–50%) by oxidation with chlorine or active manganese(IV) oxide (Scheme 3). In the ^{1}H NMR spectra of compounds **VIIa–VIIc** proton signals appeared from 3-oxobutyl substituent [δ, ppm: 1.9 ($2CH_3$), 2.2 (CH_3CO), 3.3 (CH_2)], from aromatic protons and those of ester group.

We investigated the reaction of 2-pyrazolines **I** and **XII** with 1-adamantanol. The trifluoroacetic acid was used as solvent. The system 1-adamantanol–trifluoroacetic acid was previously successfully applied to the synthesis of various adamantly-substituted azoles [5], amides [6], and aromatic hydrocarbons [7].

From the products of reaction between ester **In** and 1-adamantanol we isolated methyl 2-(1-adamantyl)-7-(3-methoxyphenyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]oct-3-enecarboxylate (**VIIIa**) in a 64% yield, whereas the reaction of ester **Ij** with 1-adamantanol afforded a mixture of pyrazoline **VIIIb** and pyrazole **IX** in a ratio 1:1.6.

IR spectra of pyrazolines **VIIIa** and **VIIIb** contain absorption bands in the 1720 (CO), 2850–2860 and 2900–

Scheme 5.



XIIa–XIIc **XIIIa–XIIIc**

XII, XIII, R = Me, R' = 4-ClC_6H_4 (**a**); R = Et, R' = 3-MeC_6H_4 (**b**), 2,4,6-$Me_3C_6H_2$ (**c**).

2910 cm^{-1} (adamantyl substituent). In the ^1H NMR spectra of these compounds protons at C^1 and C^5 give rise to doublets at 5.2 and 4.8 ppm (*J* 11 Hz) respectively, and signals from the protons of the adamantyl substituent appear at 1.7, 1.9, and 2.2 ppm.

Reactions of pyrazolines **I** with 1-adamantanol in the trifluoroacetic acid gave not only N-adamantyl-substituted pyrazolines **VIII**, but also pyrazoles, products of their oxidation apparently by air oxygen. Therefore we further used in the adamantylation pyrazoles **X** prepared by oxidation of pyrazolines **I** [8]. Reactions of pyrazoles **Xa–Xj** with 1-adamantanol in the trifluoroacetic acid at 70°C furnished esters **XIa–Xj** in up to 95% yields (Scheme 4).

The ^1H NMR spectra of pyrazoles **XIa–XIj** contain signals from adamantyl protons in the region 1.8, 2.2, and 2.3 ppm, and also signals from aromatic and ester group protons.

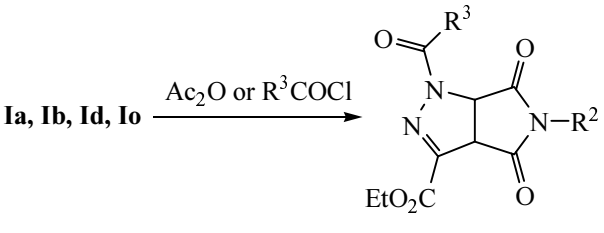
Spirocyclic pyrazolines **XII** in reaction with 1-adamantanol behave unlike bicyclic pyrazolines **I**. The reaction between esters of 6,8-dioxo-1,2,7-triazaspiro[4.4]-non-2-ene-3-carboxylic acids **XIIa–XIIc** and 1-adamantanol in the trifluoroacetic acid or in a mixture trifluoroacetic acid–dichloroethane at 70°C gave a complex mixture of substances from which by means of column chromatography we separated esters of substituted 2-(1-adamantyl)-3-(2,5-dioxotetrahydro-1*H*-pyrrol-3-ylidene)propionic acids **XIIIa–XIIIc** in 15–21% yields (Scheme 5).

In the IR spectra of compounds **XIIIa–XIIc** a strong absorption band is observed at 1720 cm^{-1} (C=O). In the ^1H NMR spectra appear doublets at 3.4 and 3.5 ppm (*J* 19 Hz) belonging to the methylene group protons of the pyrrolidine ring and doublets in the region 2.9 and 7.1 ppm (*J* 11 Hz) corresponding to the methine and the olefin protons respectively. The signals from protons of the adamantyl moiety, ester group, and aromatic ring also are observed in the spectra. The presumable mechanism of compounds **XIIIa–XIIIc** formation involves an electrophilic attack of adamantyl cation on the double bond followed by the opening of the pyrazoline ring and nitrogen elimination..

Reactions of pyrazolines **I** and **XII** with anhydrides or acyl chlorides of carboxylic acids afford their acyl derivatives. Acetic anhydride, acetyl chloride, trifluoroacetic anhydride, benzoyl chloride, and adamantanecarbonyl chloride were used as acylating agents. The latter reagent led to preparation of adamantyl-substituted heterocycles of pyrazoline series.

The reaction of esters **Ia** and **Ib** with acetic anhydride in toluene at 110°C and of ester **Io** with benzoyl chloride

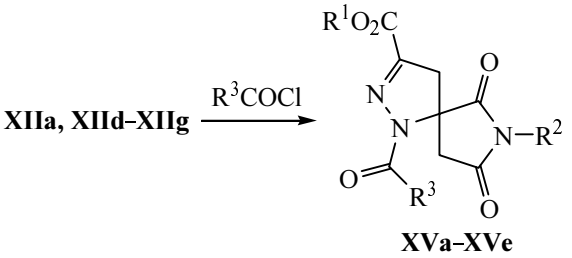
Scheme 6.



XIVa–e

I, R^1 = Et, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**), *cyclo*-C_6H_{11} (**d**), Et (**o**); **XIV**, R^3 = Me, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**); R^2 = Et, R^3 = Ph (**c**); R^3 = 1-Ad, R^2 = Ph (**d**), *cyclo*-C_6H_{11} (**e**).

Scheme 7.



XII, R^1 = Me, R^2 = 4-ClC_6H_4 (**a**), 3-Cl-4-MeC_6H_4 (**d**), 4-BrC_6H_4 (**e**); R^1 = Et, R^2 = 4-$EtOC_6H_4$ (**f**), 3-$MeOC_6H_4$ (**g**); **XV,** $R^1 = R^3$ = Me, R^2 = 3-Cl-4-MeC_6H_3 (**a**), 4-ClC_6H_4 (**b**); R^1 = Et, R^2 = 4-$EtOC_6H_4$, R^3 = Me (**c**); R^1 = Et, R^2 = 3-$MeOC_6H_4$, $R^3 = CF_3$ (**d**); R^1 = Me, R^2 = 4-BrC_6H_4, R^3 = 1-Ad (**e**).

in anhydrous toluene at 110°C gave rise to esters of substituted 1-acetyl- (**XIVa** and **XIVb**) and 1-benzoyl- (**XIVc**) -6,8-dioxo-2,3,7-triazabicyclo[3.3.0]-oct-3-ene-4-carboxylic acids in 94 and 33% yields respectively (Scheme 6). In the ^{1}H NMR spectra the doublets from the protons HC^5 and HC^1 appear respectively at 4.9, 5.9 ppm (*J* 11 Hz) (compounds **XIVa** and **XIVb**) and at 4.8, 6.0 ppm (*J* 10 Hz) (compound **XIVc**).

In reaction of compounds **Ia** and **Id** with adamantanecarbonyl chloride in toluene at 110°C esters of substituted 2-(1-adamantanoyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]-oct-3-ene-4-carboxylic acids **XIVd** and **XIVe** were obtained in up to 94% yield. The ^{1}H NMR spectrum of these compounds contained doublet signals of protons attached to C^1 and C^5 at 4.6 and 5.7 ppm (*J* 11 Hz), and also signals of adamantyl moiety at 1.8–2.2 ppm.

Reactions of esters **XIIa**, **XIId–XIIg** with acetyl chloride or trifluoroacetic anhydride in dichloromethane at 40°C furnish esters of substituted 1-acetyl- (**XVa–XVc**) and 1-trifluoroacetyl- (**XVd**) -6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylic acids in up to 97% yield. In the ^{1}H NMR spectra of these compounds doublet signals are observed from the protons of the methylene group in the pyrazoline ring at 2.9, 3.5 ppm (*J* 18 Hz) (for compounds **XVa–XVc**) and 3.1, 3.5 ppm (*J* 18 Hz) (for compound **XVd**), and also doublets from the protons of the methylene group in the pyrrolidine ring at 3.3, 3.8 ppm (*J* 19 Hz) (for compounds **XVa–XVc**) and 3.4, 3.9 ppm (*J* 18 Hz) (for compound **XVd**).

The reaction of ester **XIId** with adamantanecarbonyl chloride in anhydrous toluene for 5 h afforded methyl 1-adamantanoyl-7-(4-bromophenyl)-6,8-di-oxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (**XVe**) in a 51% yield. The structure and composition of ester **XVe** was proved by spectral data and elemental analysis. In the ^{1}H NMR spectrum the doublets from the methylene protons of the pyrazoline ring appeared at 3.17 and 3.35 ppm (*J* 18 Hz), and those from the pyrrolidine ring at 2.93 and 3.67 ppm (*J* 18 Hz). The adamantyl protons gave rise to signals at 1.8 and 2.1 ppm

EXPERIMENTAL

Elemental analyses of compounds were performed on CHN-analyzer Hewlett-Packard 185 B. Melting points of compounds were measured on a Boëtius heating block. IR spectra were recorded from 2% solutions in chloroform on a spectrophotometer UR-20. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-300 at 300 and 75 MHz respectively from solutions in $CDCl_3$. UV spectra were taken in ethanol or dichloroethane on Specord UV-VIS instrument. The purity and homogeneity of compounds and the monitoring of reaction progress were carried out by TLC on Silufol UV-254 plates. The separation by column chromatography was carried out with the use of silica gel L100-160 (100–160 μm) and L 40-100 (40–100 μm).

Esters of substituted 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylic acids IIa–IIk. Through a solution of an appropriate pyrazoline **I** in 15 ml of the freshly distilled acetone was passed a flow of gaseous HCl or HBr for 5–10 s (TLC monitoring). The solvent was evaporated, the residue was recrystallized from ethanol.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (IIa) was obtained from 0.13 g (0.4 mmol) of compound **Ia**. Yield 0.13 g (74%), mp 92–94°C. IR spectrum, cm^{-1}: 1040, 1120, 1240 s, 1380 s, 1500, 1720 v. s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, CH_3, *J* 7 Hz), 1.51 s (3H, CH_3), 1.63 s (3H, CH_3), 2.15 s (3H, CH_3), 2.85 d (1H, CH_2, *J* 17 Hz), 3.14 d (1H, CH_2, *J* 17 Hz), 4.25–4.40 m (2H, OCH_2), 4.81 d (1H, CH, *J* 11 Hz), 5.45 d (1H, CH, *J* 11 Hz), 7.23–7.53 m (5H, C_6H_5). Found, %: C 62.20; H 5.86; N 10.78. $C_{20}H_{23}N_3O_5$. Calculated, %: C 62.33; H 6.01; N 10.90.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(4-chlorophenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIb) was obtained from 0.23 g (0.7 mmol) of compound **Ib**. Yield 0.26 g (83%), mp 116–118°C. IR spectrum, cm^{-1}: 1020, 1100, 1120, 1240 s, 1310, 1380 s, 1490, 1720 v. s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, CH_3, *J* 7 Hz), 1.51 s (3H, CH_3), 1.62 s (3H, CH_3), 2.16 s (3H, CH_3), 2.86 d (1H, CH_2,

J 17 Hz), 3.12 d (1H, CH_2, *J* 17 Hz), 4.29–4.41 m (2H, OCH_2), 4.81 d (1H, CH, *J* 11 Hz), 5.44 d (1H, CH, *J* 11 Hz), 7.27 d (2 H, C_6H_4, *J* 8 Hz), 7.48 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 57.34; H 5.13; N 9.74. $C_{20}H_{22}ClN_3O_5$. Calculated, %: C 57.22; H 5.28; N 10.01.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-7-(4-methoxyphenyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]-oct-3-ene-4-carboxylate (IIc) was obtained from 0.38 g (1.2 mmol) of compound **Ic**. Yield 0.44 g (87%), mp 164–166°C. IR spectrum, cm^{-1}: 1040, 1120, 1260 s, 1300, 1380, 1470, 1530, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, CH_3, *J* 7 Hz), 1.51 s (3H, CH_3), 1.63 s (3H, CH_3), 2.14 s (3H, CH_3), 2.87 d (1H, CH_2, *J* 17 Hz), 3.11 d (1H, CH_2, *J* 17 Hz), 3.82 s (3H, OCH_3), 4.28–4.40 m (2H, OCH_2), 4.79 d (1H, CH, *J* 11 Hz), 5.41 d (1H, CH, *J* 11 Hz), 6.98 d (2H, C_6H_4, *J* 9 Hz), 7.18 d (2H, C_6H_4, *J* 9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.7, 25.4, 28.8, 32.0 (CH_3), 53.1 (C^5), 53.8 ($\underline{C}H_2COCH_3$), 55.9 (OCH_3), 60.8 ($CH_3\underline{C}H_2O$), 61.7 [$(CH_3)_2\underline{C}$–N], 65.9 (C^1), 114.9, 124.3, 128.0 (C_{arom}), 132.3 (C=N), 160.1 (C_{arom}), 161.4, 171.3, 173.6, 207.4 (CO). Found, %: C 60.52; H 6.07; N 10.12. $C_{21}H_{25}N_3O_6$. Calculated, %: C 60.72; H 6.06; N 10.10.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-cyclohexyl-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IId) was obtained from 0.37 g (1.3 mmol) of compound **Id**. Yield 0.21 g (42%), mp 108–109°C. UV spectrum (dichloroethane), λ_{max}, nm (log ε): 312.5 (4.01). IR spectrum, cm^{-1}: 1030, 1120, 1150, 1240, 1370, 1710 v.s, 2930 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.15–1.31 m (3H, C_6H_{11}), 1.38 t (3H, CH_3, *J* 7 Hz), 1.47 s (3H, CH_3), 1.60 s (3H, CH_3), 1.65–2.11 m (7H, C_6H_{11}), 2.12 s (3H, CH_3), 2.84 d (1H, CH_2, *J* 17 Hz), 3.08 d (1H, CH_2, *J* 17 Hz), 3.91– 4.01 m (1H, C_6H_{11}), 4.31–4.40 m (2H, CH_2), 4.58 d (1H, CH, *J* 11 Hz), 5.15 d (1H, CH, *J* 11 Hz). Found, %: C 61.29; H 7.28; N 10.61. $C_{20}H_{29}N_3O_5$. Calculated, %: C 61.37; H 7.47; N 10.73.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-7-(3,4-dimethylphenyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIe) was obtained from 0.38 g (1.2 mmol) of compound **Ie**. Yield 0.26 g (52%), mp 79–81°C. UV spectrum (dichloroethane), λ_{max}, nm (log ε): 315 (3.97). IR spectrum, cm^{-1}: 1010, 1120, 1240 e, 1310, 1380 e, 1530, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, CH_3, *J* 7 Hz), 1.51 e (3H, CH_3), 1.63 s (3H, CH_3), 2.15 s (3H, CH_3), 2.28 s (6H, 2 CH_3), 2.86 d (1H, CH_2, *J* 17 Hz), 3.12 d (1H, CH_2, *J* 17 Hz), 4.31–4.42 m (2H, OCH_2), 4.79 d (1H, CH, *J* 11 Hz), 5.41 d (1H, CH, *J* 11 Hz), 6.97 d (1H, C_6H_3, *J* 8 Hz), 7.05 s (1H, C_6H_3), 7.23 d (1H, C_6H_3, *J* 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.7, 19.9, 20.2, 25.4, 28.8, 32.0 (CH_3), 53.1 (C^5), 53.8 ($\underline{C}H_2COCH_3$), 60.8 ($CH_3\underline{C}H_2O$), 61.7 [$(CH_3)_2\underline{C}$–N], 66.7 (C^1), 124.1, 127.7, 129.1, 130.7 (C_{arom}), 132.2 ($\underline{C}$=N), 138.2 (C_{arom}), 161.3 (C_{arom}), 161.4, 171.5, 174.0, 207.6 (CO). Found, %: C 64.06; H 6.60; N 10.06. $C_{22}H_{27}N_3O_5$. Calculated, %: C 63.91; H 6.58; N 10.16.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(4-fluorophenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIf) was obtained from 0.30 g (1 mmol) of compound **If**. Yield 0.34 g (86%), mp 131–132°C. IR spectrum, cm^{-1}: 1030, 1120, 1240 s, 1300, 1380 s, 1510, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, CH_3, *J* 7 Hz), 1.51 s (3H, CH_3), 1.63 s (3H, CH_3), 2.15 s (3H, CH_3), 2.86 d (1H, CH_2, *J* 17 Hz), 3.12 d (1H, CH_2, *J* 17 Hz), 4.29–4.41 m (2H, OCH_2), 4.80 d (1H, CH, *J* 11 Hz), 5.44 d (1H, CH, *J* 11 Hz), 7.14–7.26 m (4H, C_6H_4). Found, %: C 59.53; H 5.65; N 10.25. $C_{20}H_{22}FN_3O_5$. Calculated, %: C 59.55; H 5.50; N 10.42.

Methyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(4-chlorophenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIg) was obtained from 0.50 g (1.6 mmol) of compound **Ig.** Yield 0.51 g (77%), mp 163–164°C. IR spectrum, cm^{-1}: 1020, 1100, 1130, 1240 s, 1310, 1380 s, 1470, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 s (3H, CH_3), 1.64 s (3H, CH_3), 2.15 s (3H, CH_3), 2.86 d (1H, CH_2, *J* 17 Hz), 3.11 d (1H, CH_2, *J* 17 Hz), 3.89 s (3H, OCH_3), 4.81 d (1H, CH, *J* 11 Hz), 5.47 d (1H, CH, *J* 11 Hz), 7.26 d (2H, C_6H_4, *J* 8 Hz), 7.44 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 56.13; H 4.76; N 10.29. $C_{19}H_{20}ClN_3O_5$. Calculated, %: C 56.23; H 4.97; N 10.35.

Methyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]-oct-3-ene-4-carboxylate (IIh) was obtained from 0.31 g (1 mmol) of compound **Ih**. Yield 0.32 g (76%), mp 168–169°C. IR spectrum, cm^{-1}: 1020, 1120, 1200, 1380 s, 1450, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 s (3H, CH_3), 1.63 s (3H, CH_3), 2.15 s (3H, CH_3), 2.38 s (3H, CH_3), 2.87 d (1H, CH_2, *J* 17 Hz), 3.12 d (1H, CH_2, *J* 17 Hz), 3.89 s (3H, OCH_3), 4.79 d (1H, CH, *J* 11 Hz), 5.43 d (1H, CH, *J* 11 Hz), 7.15 d (2H, C_6H_4, *J* 8 Hz), 7.27 d (2H, C_6H_4, *J* 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.6, 25.4, 28.8, 31.9 (CH_3), 51.9 (C^5), 52.3 (CH_3O), 53.8 ($\underline{C}H_2COCH_3$), 60.8 [$(CH_3)_2\underline{C}$–N], 66.0 (C^1), 126.5, 129.1, 130.2 (C_{arom}), 131.8 (C=N),

139.4 (C_{arom}), 161.9, 171.3, 173.4, 207.4 (CO). Found, %: C 62.41; H 5.88; N 10.83. $C_{20}H_{23}N_3O_5$. Calculated, %: C 62.33; H 6.01; N 10.90.

Methyl 7-(4-bromophenyl)-2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]-oct-3-ene-4-carboxylate (IIi) was obtained from 0.47 g (1.3 mmol) of compound **Ii**. Yield 0.51 g (84%), mp 113–115°C. IR spectrum, cm^{-1}: 1020, 1090, 1130, 1240 s, 1310, 1380 s, 1490, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 s (3H, CH_3), 1.63 s (3H, CH_3), 2.15 s (3H, CH_3), 2.85 d (1H, CH_2, *J* 17 Hz), 3.11 d (1H, CH_2, *J* 17 Hz), 3.88 s (3H, OCH_3), 4.81 d (1H, CH, *J* 11 Hz), 5.43 d (1H, CH, *J* 11 Hz), 7.15 d (2H, C_6H_4, *J* 8 Hz), 7.61 d (2H, C_6H_4, *J* 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.7, 28.2, 31.1 (CH_3), 51.9 (C^5), 52.3 (CH_3O), 53.8 ($\underline{C}H_2COCH_3$), 60.8 [$(CH_3)_2\underline{C}$–N], 66.8 (C^1), 123.2, 128.3, 130.8 (C_{arom}), 131.6 (C=N), 132.9 (C_{arom}), 161.8, 170.8, 173.0, 207.3 (CO). Found, %: C 50.73; H 4.22; N 9.41. $C_{19}H_{20}BrN_3O_5$. Calculated, %: C 50.68; H 4.48; N 9.33.

Methyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(3,5-dichlorophenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIj) was obtained from 0.61 g (1.8 mmol) of compound **Ij**. Yield 0.72 g (91%), mp 163–164°C. IR spectrum, cm^{-1}: 1130, 1240 s, 1310, 1370 s, 1440, 1580, 1730 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 s (3H, CH_3), 1.61 s (3H, CH_3), 2.13 s (3H, CH_3), 2.84 d (1H, CH_2, *J* 17 Hz), 3.09 d (1H, CH_2, *J* 17 Hz), 3.87 s (3H, OCH_3), 4.81 d (1H, CH, *J* 11 Hz), 5.47 d (1H, CH, *J* 11 Hz), 7.26 s (2H, C_6H_3), 7.40 s (1H, C_6H_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.4, 29.0, 31.8 (CH_3), 52.7 (C^5), 53.1 (CH_3O), 53.8 ($\underline{C}H_2COCH_3$), 60.8 [$(CH_3)_2\underline{C}$–N], 66.8 (C^1), 125.3, 129.5 (C_{arom}), 131.9 (C=N), 133.8, 135.7 (C_{arom}), 161.9, 170.5, 173.2, 207.4 (CO). Found, %: C 51.59; H 4.31; N 9.33. $C_{19}H_{19}Cl_2N_3O_5$. Calculated, %: C 51.83; H 4.35; N 9.54.

Methyl 2-(1,1-dimethyl-3-oxobutyl)-7-(4-methoxyphenyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIk) was obtained from 0.43 g (1.4 mmol) of compound **Ik**. Yield 0.53 g (94%), mp 170–172°C. IR spectrum, cm^{-1}: 1040, 1120, 1260 s, 1310, 1390, 1450, 1520, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 s (3H, CH_3), 1.63 s (3H, CH_3), 2.14 s (3H, CH_3), 2.86 d (1H, CH_2, *J* 17 Hz), 3.11 d (1H, CH_2, *J* 17 Hz), 3.83 C (3H, OCH_3), 3.88 s (3H, OCH_3), 4.79 d (1H, CH, *J* 11 Hz), 5.42 d (1H, CH, *J* 11 Hz), 6.97 d (2H, C_6H_4, *J* 8 Hz), 7.18 d (2H, C_6H_4, *J* 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.4, 28.8, 32.0 (CH_3), 52.6 (C^5), 53.0 (CH_3O), 53.8 ($\underline{C}H_2COCH_3$), 55.9 (CH_3O), 60.7 [$(CH_3)_2\underline{C}$–N], 66.7 (C^1), 114.9, 124.3, 128.0 (C_{arom}), 131.8 (C=N), 160.1 (C_{arom}), 161.9, 171.4, 173.5, 207.3 (CO). Found, %: C 59.91, H 5.59, N 10.34. $C_{20}H_{23}N_3O_6$. Calculated, %: C 59.84, H 5.77, N 10.47.

Reaction of esters of substituted 6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids Ih, Ik, and Il with 2-butanone in the presence of HBr. Through a solution of an appropriate pyrazoline **I** in 2-butanone was passed a stream of gaseous HBr for 10–15 s. The mixture obtained was heated at 70°C for 8 h (or was maintained at room temperature for 24–32 h). The solvent was distilled off in a vacuum. The reaction products were isolated by column chromatography (eluent hexane–ethyl acetate, 2:1 by volume).

Methyl 2-(1-methyl-3-oxo-1-ethylpentyl)-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo-[3.3.0]-oct-3-ene-4-carboxylate (IIIa). From 0.30 g (1 mmol) of compoundя **Ih** was obtained 0.065 g (17%) of oily ester **IIIa** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 910, 1120, 1230, 1320, 1380, 1450, 1540, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.91 t (3H, CH_3, *J* 7 Hz), 0.99 t (3H, CH_3, *J* 7 Hz), 1.61 s (3H, CH_3), 1.62–1.69 m (1H, alkyl), 1.91–2.02 m (1H, alkyl), 2.38 s (3H, CH_3), 2.39–2.48 m (2H, alkyl), 2.72 d (1H, CH_2, *J* 17 Hz), 3.06 d (1H, CH_2, *J* 17 Hz), 3.85 s (3H, OCH_3), 4.81 d (1H, CH, *J* 12 Hz), 5.55 d (1H, CH, *J* 12 Hz), 7.12 d (2H, C_6H_4, *J* 8 Hz), 7.25 d (2H, C_6H_4, *J* 8 Hz); minor diastereomer: 0.91 t (3H, CH_3, *J* 7 Hz), 0.99 t (3H, CH_3, *J* 7 Hz), 1.52 s (3H, CH_3), 1.62–1.69 m (1H, alkyl), 1.91–2.02 m (1H, alkyl), 2.38 s (3H, CH_3), 2.39–2.48 m (2H, alkyl), 2.89 d (1H, CH_2, *J* 17 Hz), 2.99 d (1H, CH_2, *J* 17 Hz), 3.86 s (3H, OCH_3), 4.78 d (1H, CH, *J* 11 Hz), 5.37 d (1H, CH, *J* 11 Hz), 7.12 d (2H, C_6H_4, *J* 8 Hz), 7.25 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 63.78; H 6.64; N 9.97. $C_{22}H_{27}N_3O_5$. Calculated, %: C 63.91; H 6.58; N 10.16.

Methyl 2-(1-methyl-3-oxo-1-ethylpentyl)-6,8-dioxo-7-(4-ethoxyphenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIIb). From 0.30 g (0.95 mmol) of compound **Il** was obtained 0.08 g (18%) of oily ester **IIIb** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 910, 1140, 1230, 1320, 1380, 1450, 1560, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.91 t (3H, CH_3, *J* 7 Hz), 0.99 t (3H, CH_3, *J* 7 Hz), 1.41 t (3H, CH_3, *J* 7 Hz), 1.61 s (3H, CH_3), 1.64–1.68 m (1H, alkyl), 1.89–2.03 m (1H, alkyl), 2.41–2.48 m (2H, alkyl), 2.72 d (1H, CH_2, *J* 17 Hz), 3.06 d (1H, CH_2, *J* 17 Hz), 3.85 s (3H,

OCH_3), 4.10 q (2H, OCH_2, *J* 7 Hz), 4.81 d (1H, CH, *J* 12 Hz), 5.57 d (1H, CH, *J* 12 Hz), 6.94 d (2H, C_6H_4, *J* 8 Hz), 7.15 d (2H, C_6H_4, *J* 8 Hz); minor diastereomer: 0.91 t (3H, CH_3, *J* 7 Hz), 0.99 t (3H, CH_3, *J* 7 Hz), 1.52 s (3H, CH_3), 1.64–1.68 m (1H, alkyl), 1.89–2.03 m (1H, alkyl), 2.41–2.48 m (2H, alkyl), 2.89 d (1H, CH_2, *J* 17 Hz), 2.98 d (1H, CH_2, *J* 17 Hz), 3.86 s (3H, OCH_3), 4.10 q (2H, OCH_2, *J* 7 Hz), 4.78 d (1H, CH, *J* 11 Hz), 5.38 d (1H, CH, *J* 11 Hz), 6.94 d (2H, C_6H_4, *J* 8 Hz), 7.15 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 62.11; H 6.73; N 9.32. $C_{23}H_{29}N_3O_6$. Calculated, %: C 62.29; H 6.59; N 9.47.

Methyl 2-(1-methyl-3-oxo-1-ethylpentyl)-6,8-dioxo-7-(4-methoxyphenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IIIc). From 0.30 g (1.0 mmol) of compound **Ik** was obtained 0.11 g (27%) of oily ester **IIIc** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 930, 1040, 1110, 1220 s, 1300, 1390, 1440, 1720 v.s, 3050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.85 t (3H, CH_3, *J* 7 Hz), 1.00 t (3H, CH_3, *J* 7 Hz), 1.61 s (3H, CH_3), 1.64–1.68 m (1H, alkyl), 1.91–2.05 m (1H, alkyl), 2.38–2.49 m (2H, alkyl), 2.71 d (1H, CH_2, *J* 17 Hz), 3.05 d (1H, CH_2, *J* 17 Hz), 3.82 s (3H, OCH_3), 3.85 s (3H, OCH_3), 4.81 d (1H, CH, *J* 12 Hz), 5.53 d (1H, CH, *J* 12 Hz), 6.95 d (2H, C_6H_4, *J* 9 Hz), 7.15 d (2H, C_6H_4, *J* 9 Hz); minor diastereomer: 0.85 t (3H, CH_3, *J* 7 Hz), 1.00 t (3H, CH_3, *J* 7 Hz), 1.50 s (3H, CH_3), 1.64–1.68 m (1H, alkyl), 1.91–2.05 m (1H, alkyl), 2.38–2.49 m (2H, alkyl), 2.88 d (1H, CH_2, *J* 17 Hz), 2.99 d (1H, CH_2, *J* 17 Hz), 3.82 s (3H, OCH_3), 3.86 s (3H, OCH_3), 4.76 d (1H, CH, *J* 11 Hz), 5.35 d (1H, CH, *J* 11 Hz), 6.95 d (2H, C_6H_4, *J* 9 Hz), 7.15 d (2H, C_6H_4, *J* 9 Hz). Found, %: C 61.74; H 6.25; N 9.67. $C_{22}H_{27}N_3O_6$. Calculated, %: C 61.53; H 6.34; N 9.78.

Methyl 2-(1-methyl-3-oxo-1-propylhexyl)-6,8-dioxo-7-(4-ethoxyphenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (IV). A solution of 0.30 g (0.95 mmol) of compound **II** in 10 ml of 2-pentanone was saturated with gaseous HBr for 20 s. The solution obtained was heated at 70°C for 3 h and then was maintained for 12 h at room temperature. The solvent was distilled off in a vacuum, the residue was subjected to column chromatography on silica gel (eluent hexane–ethyl acetate, 2.3:1 by volume). We obtained 0.09 g (21%) of oily ester **IV** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 1040, 1120, 1260, 1380, 1440, 1520, 1720 v.s, 2980. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.80–0.91 m (6H, alkyl), 1.21–1.32 m (3H, alkyl), 1.37 t (3H, CH_3, *J* 7 Hz), 1.49–1.58 m (3H, alkyl), 1.61 s (3H, CH_3), 1.80–1.91 m (1H, alkyl), 2.28–2.39 m (2H, alkyl), 2.68 d (1H, CH_2, *J* 18 Hz), 3.04 d (1H, CH_2, *J* 18 Hz), 3.81 s (3H, OCH_3), 3.99 q (2H, OCH_2, *J* 7 Hz), 4.75 d (1H, CH, *J* 11 Hz), 5.53 d (1H, CH, *J* 11 Hz), 6.91 d (2H, C_6H_4, *J* 8 Hz), 7.09 d (2H, C_6H_4, *J* 8 Hz); minor diastereomer: 0.80–0.91 m (6H, alkyl), 1.21–1.32 m (3H, alkyl), 1.37 t (3H, CH_3, *J* 7 Hz), 1.49–1.58 m (3H, alkyl), 1.52 s (3H, CH_3), 1.80–1.91 m (1H, alkyl), 2.28–2.39 m (2H, alkyl), 2.87 d (1H, CH_2, *J* 16 Hz), 2.95 d (1H, CH_2, *J* 16 Hz), 3.82 s (3H, OCH_3), 3.99 q (2H, OCH_2, *J* 7 Hz), 4.72 d (1H, CH, *J* 11 Hz), 5.34 d (1H, CH, *J* 11 Hz), 6.91 d (2H, C_6H_4, *J* 8 Hz), 7.09 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 63.54; H 6.95; N 8.54. $C_{25}H_{33}N_3O_6$. Calculated, %: C 63.68; H 7.05; N 8.91.

Methyl 2-(1-butyl-1-methyl-3-oxoheptyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (V). A solution of 0.30 g (1.1 mmol) of compound **Im** in 10 ml of 2-hexanone was saturated with gaseous HBr for 30 s. The solution obtained was heated at 70°C for 3 h and then was maintained for 12 h at room temperature. The solvent was distilled off under reduced pressure, the residue was subjected to column chromatography on silica gel (eluent hexane–ethyl acetate, 3:1 by volume). We obtained 0.07 g (15%) of oily ester **V** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 1050, 1110, 1260, 1360, 1450, 1520, 1720 v.s, 2990. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.83–0.94 m (6H, alkyl), 1.23–1.30 m (3H, alkyl), 1.49–1.58 m (4H, alkyl), 1.63 s (3H, CH_3), 1.80–1.91 m (1H, alkyl), 2.28–2.39 m (2H, alkyl), 2.68 d (1H, CH_2, *J* 18 Hz), 3.04 d (1H, CH_2, *J* 18 Hz), 3.81 s (3H, OCH_3), 4.75 d (1H, CH, *J* 11 Hz), 5.53 d (1H, CH, *J* 11 Hz), 7.21–7.52 m (5H, C_6H_5); minor diastereomer: 0.83–0.94 m (6H, alkyl), 1.23–1.30 m (3H, alkyl), 1.49–1.58 m (4H, alkyl), 1.51 s (3H, CH_3), 1.80–1.91 m (1H, alkyl), 2.28–2.39 m (2H, alkyl), 2.87 d (1H, CH_2, *J* 16 Hz), 2.95 d (1H, CH_2, *J* 16 Hz), 3.82 x (3H, OCH_3), 4.72 d (1H, CH, *J* 11 Hz), 5.34 d (1H, CH, *J* 11 Hz), 7.21–7.52 m (5H, C_6H_5). Found, %: C 65.67; H 7.58; N 9.11. $C_{25}H_{33}N_3O_5$. Calculated, %: C 65.91; H 7.30; N 9.22.

Methyl 2-(1-heptyl-1-methyl-3-oxodecyl)-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-4-carboxylate (VI). A solution of 0.30 g (1.0 mmol) of compound **Ih** in 8 ml of 2-nonanone was saturated with gaseous HBr at 60°C for 40 s. The solution obtained was heated for 5 h at 100°C, and then it was left standing for 24 h at room temperature. The solvent was distilled

off in a vacuum, the residue was subjected to column chromatography on silica gel (eluent hexane–ethyl acetate, 4.5:1 by volume). We obtained 0.04 g (7%) of oily ester **VI** as a mixture of two diastereomers in a ratio 2:1. IR spectrum, cm^{-1}: 1120, 1190, 1310, 1380 s, 1440, 1540, 1720 v.s, 2930 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: major diastereomer: 0.82–0.93 m (6H, alkyl), 1.22–1.30 m (20H, alkyl), 1.42–1.63 m (2H, alkyl), 1.65 s (3H, CH_3), 2.29–2.42 m (3H, alkyl), 2.43 s (3H, CH_3), 2.71 d (1H, CH_2, *J* 18 Hz), 3.10 d (1H, CH_2, *J* 18 Hz), 3.86 s (3H, OCH_3), 4.81 d (1H, CH, *J* 12 Hz), 5.57 d (1H, CH, *J* 12 Hz), 7.12 d (2H, C_6H_4, *J* 8 Hz), 7.26 d (2H, C_6H_4, *J* 8 Hz); minor diastereomer: 0.82–0.93 m (6H, alkyl), 1.22–1.30 m (20H, alkyl), 1.42–1.63 m (2H, alkyl), 1.52 s (3H, CH_3), 2.29–2.42 m (3H, alkyl), 2.43 s (3H, CH_3), 2.92 d (1H, CH_2, *J* 17 Hz), 3.01 d (1H, CH_2, *J* 17 Hz), 3.88 s (3H, OCH_3), 4.77 d (1H, CH, *J* 12 Hz), 5.41 d (1H, CH, *J* 12 Hz), 7.12 d (2H, C_6H_4, *J* 8 Hz), 7.26 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 69.22; H 8.71; N 7.53. $C_{32}H_{47}N_3O_5$. Calculated, %: C 69.41; H 8.55; N 7.59.

Esters of substituted 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]-octa-1(5),3-diene-4-carboxylic acids VIIa–VIIc. Through a solution of an appropriate pyrazoline **IIa**, **IIb**, and **IIe** in chloroform was passed a stream of chlorine till the solution turned light yellow. The reaction flask was stoppered and left standing at room temperature for 2 h. The solvent was evaporated, the residue was recrystallized from ethanol.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (VIIa) was obtained from 0.48 g (1.2 mmol) of compound **IIa**. Yield 0.23 g (48%), mp 122–123°C. IR spectrum, cm^{-1}: 1020, 1090, 1130, 1280, 1360 s, 1510, 1730 v.s, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 t (3H, CH_3, *J* 7 Hz), 1.85 s (6H, $2CH_3$), 2.21 s (3H, CH_3), 3.32 s (2H, CH_2), 4.47 q (2H, OCH_2, *J* 7 Hz), 7.36–7.51 m (5H, C_6H_5). Found, %: C 62.63; H 5.34; N 10.78. $C_{20}H_{21}N_3O_5$. Calculated, %: C 62.66; H 5.52; N 10.96.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-6,8-dioxo-7-(4-chlorophenyl)-2,3,7-triazabicyclo-[3.3.0]octa-1(5),3-diene-4-carboxylate (VIIb) was obtained from 0.69 g (1.7 mmol) of compound **IIb**. Yield 0.35 g (51%), mp 134–135°C. IR spectrum, cm^{-1}: 1020, 1080, 1130, 1280, 1350 C, 1490, 1730 v.s, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_3, *J* 7 Hz), 1.85 s (6H, CH_3), 2.20 s (3H, CH_3), 3.31 s (2H, CH_2), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.33 d (2H, C_6H_4, *J* 8 Hz), 7.48 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 57.36; H 4.74; N 9.87. $C_{20}H_{20}ClN_3O_5$. Calculated, %: C 57.49; H 4.82; N 10.06.

Ethyl 2-(1,1-dimethyl-3-oxobutyl)-7-(3,4-dimethylphenyl)-6,8-dioxo-2,3,7-triazabicyclo-[3.3.0]octa-1(5),3-diene-4-carboxylate (VIIc). To a solution of 0.40 g (1 mmol) of compound **IIe** in 15 ml of anhydrous acetone was added at stirring 1.04 g (12 mmol) of active manganese(IV) oxide (γ-MnO_2). The dispersion was stirred for 7 h at room temperature (TLC monitoring), MnO_2 was filtered off, washed twice with dichloromethane, the solvent was distilled off from the combined filtrates, and the residue was subjected to column chromatography. Yield 0.16 g (39%), mp 112–113°C. IR spectrum, cm^{-1}: 1020, 1090, 1140, 1280, 1360 s, 1460, 1520, 1730 v.s, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 t (3H, CH_3, *J* 7 Hz), 1.85 s (6H, $2CH_3$), 2.20 s (3H, CH_3), 2.32 s (6H, $2CH_3$), 3.32 s (2H, CH_2), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.03 d (1H, C_6H_3, *J* 8 Hz), 7.11 C (1H, C_6H_3), 7.26 d (1H, C_6H_3, *J* 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 19.9, 20.2, 28.0, 31.8 (CH_3), 52.4 ($\underline{C}H_2COCH_3$), 62.3 ($CH_3\underline{C}H_2O$), 64.9 [–N–$\underline{C}(CH_3)_2$], 124.0 (C^5), 125.0, 128.6, 130.6, 131.3, 136.8, 138.4 (C_{arom}), 139.0 (C^1), 157.5, 159.4, 160.0, 204.9 (CO). Found, %: C 64.09; H 6.18; N 10.07. $C_{22}H_{25}N_3O_5$. Calculated, %: C 64.22; H 6.12; N 10.21.

Methyl 2-(1-adamantyl)-7-(3-methoxyphenyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (VIIIa). To a solution of 0.20 g (0.66 mmol) of compound **In** in 6 ml of trifluoroacetic acid was added 0.15 g (1 mmol) of 1-adamantanol. The mixture was stirred at 70°C for 2 h (TLC monitoring). The solvent was distilled off, the residue was recrystallized from ethanol. Yield 0.15 g (52%), mp 214–216°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.73 br.s (6H, Ad), 1.92–2.00 m (3H, Ad), 2.15–2.22 m (6H, Ad), 3.81 s (3H, OCH_3), 3.90 s (3H, OCH_3), 4.77 d (1H, CH, *J* 11 Hz), 5.19 d (1H, CH, *J* 11 Hz), 6.80 d (1H, C_6H_4, *J* 2 Hz), 6.85 d (1H, C_6H_4, *J* 8 Hz), 6.96 d.d (1H, C_6H_4, *J* 8 and 2 Hz), 7.37 t (1H, C_6H_4, *J* 8 Hz). Found, %: C 65.76; H 6.29; N 9.69. $C_{24}H_{27}N_3O_5$. Calculated, %: C 65.89; H 6.22; N 9.60.

Reaction of pyrazoline (Ij) with 1-adamantanol. To a solution of 0.25 g (0.7 mmol) of estera **Ij** in 5 ml of trifluoroacetic acid was added 0.17 g (1.1 mmol) of 1-adamantanol. The mixture was stirred under argon at 70°C for 4 h (TLC monitoring). The solvent was distilled off, the residue was separated by column chromatography. First fraction: 0.06 g (17%) of **methyl 2-(1-adamantyl)-6,8-dioxo-7-(3,5-dichlorophenyl)-2,3,7-triazabi-**

cyclo[3.3.0]-oct-3-ene-4-carboxylate (VIIIb), mp 206–208°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.72 br.s (6H, Ad), 1.90–1.99 m (3H, Ad), 2.12–2.23 m (6H, Ad), 3.91 s (3H, OCH_3), 4.79 d (1H, CH, *J* 11 Hz), 5.21 d (1H, CH, *J* 11 Hz), 7.28 s (2H, C_6H_3), 7.41 s (1H, C_6H_3). Found, %: C 57.86; H 4.94; N 8.71. $C_{23}H_{23}Cl_2N_3O_4$. Calculated, %: C 57.99; H 4.87; N 8.82. Second fraction: 0.09 g (27%)of **methyl 2-(1-adamantyl)-6,8-dioxo-7-(3,5-dichlorophenyl)-2,3,7-triazabicyclo[3.3.0]-octa-1(5),3-diene-4-carboxylate (IX)**, mp 190–192°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 br.s (6H, Ad), 2.31 br.s (3H, Ad), 2.39 br.s (6H, Ad), 4.03 s (3H, OCH_3), 7.37 s (2H, C_6H_3), 7.40 s (1H, C_6H_3). Found, %: C 58.08; H 4.44; N 8.70. $C_{23}H_{21}Cl_2N_3O_4$. Calculated, %: C 58.24; H 4.46; N 8.86.

Esters of substituted 2-(1-adamantyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylic acids XIa–XIj. To a solution of an appropriate pyrazole **X** in trifluoroacetic acid was added 1-adamantanol in 1.5-fold excess. The mixture was stirred at 70°C for 2 h. The solvent was distilled off in a vacuum, and the residue was recrystallized from ethanol.

Methyl 2-(1-adamantyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIa) was obtained from 2.4 g (8.8 mmol) of compound **Xa** and 2.01 g (13.3 mmol) of 1-adamantanol in 10 ml of trifluoroacetic acid. Yield 2.8 g (78%), mp 189–191°C. UV spectrum (dichloroethane), λ_{max}, nm (log ε): 270 (3.65). IR spectrum, cm^{-1}: 1040, 1090, 1150, 1280, 1360, 1460, 1510, 1600, 1720 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.42 br.s (6H, Ad), 4.02 s (3H, OCH_3), 7.36–7.53 m (5H, C_6H_5). Found, %: C 68.28; H 5.73; N 10.40. $C_{23}H_{23}N_3O_4$. Calculated, %: C 68.13; H 5.72; N 10.36.

Methyl 2-(1-adamantyl)-6,8-dioxo-7-(4-ethylphenyl)-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIb) was obtained from 2.5 g (8.4 mmol) of compound **Xb** and 1.8 g (12 mmol) of 1-adamantanol in 10 ml of trifluoroacetic acid. Yield 3.2 g (88%), mp 178–179°C. IR spectrum, cm^{-1}: 1100, 1140, 1290, 1360 s, 1460, 1520, 1720 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 t (3H, CH_3, *J* 7 Hz), 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.41 br.s (6H, Ad), 2.71 q (2H, CH_2, *J* 7 Hz), 4.02 s (3H, OCH_3), 7.27 d (2H, C_6H_4, *J* 8 Hz), 7.32 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 69.14; H 6.28; N 9.83. $C_{25}H_{27}N_3O_4$. Calculated, %: C 69.27; H 6.28; N 9.69.

Methyl 2-(1-adamantyl)-6,8-dioxo-7-(4-fluorophenyl)-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIc) was obtained from 0.46 g (1.6 mmol) of compound **Xc** and 0.36 g (2.4 mmol) of 1-adamantanol in 4 ml of trifluoroacetic acid. Yield 0.63 g (93%), mp 197–198°C. IR spectrum, cm^{-1}: 1020, 1040, 1090, 1140, 1280, 1380, 1470, 1500, 1730 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 br.s (6H, Ad), 2.30 s (3H, Ad), 2.39 br.s (6H, Ad), 4.03 s (3H, OCH_3), 7.01–7.37 m (4H, C_6H_4). Found, %: C 65.07; H 5.34; N 9.63. $C_{23}H_{22}FN_3O_4$. Calculated, %: C 65.24; H 5.24; N 9.92.

Ethyl 2-(1-adamantyl)-7-(4-bromo-3-methylphenyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]-octa-1(5),3-diene-4-carboxylate (XId) was obtained from 2.3 g (6 mmol) of compound **Xd** and 1.4 g (9 mmol) of 1-adamantanol in 8 ml of trifluoroacetic acid. Yield of ester **XId** 2.2 g (72%), mp 179–181°C. IR spectrum, cm^{-1}: 940, 1040, 1100, 1140, 1280, 1350 s, 1480, 1720 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7 Hz), 1.82 br.s (6H, Ad), 2.28 s (3H, Ad), 2.44 br.s (6H, Ad), 2.50 s (3H, CH_3), 4.49 q (2H, OCH_2, *J* 7 Hz), 7.08 d.d (1H, C_6H_3, *J* 3 and 8 Hz), 7.27 d (1H, C_6H_3, *J* 3 Hz), 7.65 d (1H, C_6H_3, *J* 8 Hz). Found, %: C 58.78; H 5.22; N 8.10. $C_{25}H_{26}BrN_3O_4$. Calculated, %: C 58.60; H 5.11; N 8.20.

Ethyl 2-(1-adamantyl)-6,8-dioxo-7-cyclohexyl-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIe) was obtained from 2.64 g (9.1 mmol) of compound **Xe** and 2.07 g (13.6 mmol) of 1-adamantanol in 10 ml of trifluoroacetic acid. Yield 3.47 g (90%), mp 137–139°C. UV spectrum (dichloro-ethene), λ_{max}, nm (log e): 274 (3.59). IR spectrum, cm^{-1}: 900, 950, 1010, 1080, 1140, 1270, 1330 s, 1450, 1520, 1720 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21–1.27 m (3H, Ad), 1.44 t (3H, CH_3, *J* 7 Hz), 1.71–1.87 m (11H, Ad+C_6H_{11}), 2.08–2.35 m (11H, Ad+C_6H_{11}), 4.92–5.03 m (1H, C_6H_{11}), 4.45 q (2H, OCH_2, *J* 7 Hz). Found, %: C 67.68; H 7.38; N 9.85. $C_{24}H_{31}N_3O_4$. Calculated, %: C 67.74; H 7.34; N 9.87.

Ethyl 2-(1-adamantyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIf) was obtained from 1.27 g (4.4 mmol) of compound **Xf** and 1.02 g (6.7 mmol) of 1-adamantanol in 7 ml of trifluoroacetic acid. Yield 1.7 g (91%), mp 177–178°C. IR spectrum, cm^{-1}: 1040, 1090, 1140, 1280, 1360, 1470, 1500, 1590, 1720 v.s, 2920 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7 Hz), 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.42 br.s (6H, Ad), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.36–7.53 m (5H, C_6H_5). Found, %: C 68.68; H 5.93; N 9.86. $C_{24}H_{25}N_3O_4$. Calculated, %: C 68.72; H 6.01; N 10.02.

Ethyl 2-(1-adamantyl)-7-(4-tolyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIg) was obtained from 0.80 g (2.7 mmol) of compound **Xg** and 0.61 g (4.05 mmol) of 1-adamantanol in 5 ml of trifluoroacetic acid. Yield 0.90 g (78%), mp 173–174°C. IR spectrum, cm^{-1}: 1030, 1100, 1140, 1280, 1340, 1470, 1520, 1590, 1720 v.s, 2940 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7 Hz), 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.41 br.s (6H, Ad), 2.44 s (3H, CH_3), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.23 d (2H, C_6H_4, *J* 8 Hz), 7.30 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 69.44; H 6.28; N 9.84. $C_{25}H_{27}N_3O_4$. Calculated, %: C 69.27; H 6.28; N 9.69.

Ethyl 2-(1-adamantyl)-6,8-dioxo-7-(4-chlorophenyl)-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIh) was obtained from 0.60 g (1.9 mmol) of compound **Xh** and 0.43 g (2.8 mmol) of 1-adamantanol in 5 ml of trifluoroacetic acid. Yield 0.74 g (87%), mp 193–194°C. IR spectrum, cm^{-1}: 920, 1030, 1070, 1100, 1140, 1280, 1340, 1470, 1590, 1720 v.s, 2940 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7 Hz), 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.40 br.s (6H, Ad), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.29 d (2H, C_6H_4, *J* 9 Hz), 7.47 d (2H, C_6H_4, *J* 9 Hz). Found, %: C 63.49; H 5.19; N 9.43. $C_{24}H_{24}ClN_3O_4$. Calculated, %: C 63.51; H 5.33; N 9.26.

Ethyl 2-(1-adamantyl)-7-(4-bromophenyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIi) was obtained from 0.66 g (1.8 mmol) of compound **Xi** and 0.41 g (2.7 mmol) of 1-adamantanol in 5 ml of trifluoroacetic acid. Yield 0.78 g (87%), mp 186–187°C. IR spectrum, cm^{-1}: 930, 980, 1020, 1090, 1140, 1280, 1350, 1470, 1590, 1720 v.s, 2930 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7 Hz), 1.81 br.s (6H, Ad), 2.30 s (3H, Ad), 2.40 br.s (6H, Ad), 4.48 q (2H, OCH_2, *J* 7 Hz), 7.27 d (2H, C_6H_4, *J* 9 Hz), 7.62 d (2H, C_6H_4, *J* 9 Hz). Found, %: C 57.85; H 4.84; N 8.31. $C_{24}H_{24}BrN_3O_4$. Calculated, %: C 57.84; H 4.85; N 8.43.

Ethyl 2-(1-adamantyl)-6,8-dioxo-7-(4-ethylphenyl)-2,3,7-triazabicyclo[3.3.0]octa-1(5),3-diene-4-carboxylate (XIj) was obtained from 2.3 g (7.4 mmol) of compound **Xj** and 1.5 g (10 mmol) of 1-adamantanol in 9 ml of trifluoroacetic acid. Yield 2.8 g (85%), mp 153°C. IR spectrum, cm^{-1}: 1090, 1140, 1280, 1360 s, 1460, 1520, 1720 v.s, 2920 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (3H, CH_3, *J* 7 Hz), 1.45 t (3H, CH_3, *J* 7 Hz), 1.80 br.s (6H, Ad), 2.29 s (3H, Ad), 2.41 br.s (6H, Ad), 2.70 q (2H, CH_2, *J* 7 Hz), 4.47 q (2H, OCH_2, *J* 7 Hz), 7.26 d (2H, C_6H_4, *J* 8 Hz), 7.32 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 69.68; H 6.56; N 9.56. $C_{26}H_{29}N_3O_4$. Calculated, %: C 68.78; H 6.53; N 9.39.

Esters of substituted 2-(1-adamantyl)-3-(2,5-dioxotetrahydro-1*H*-pyrrol-3-ylidene)-propionic acids (XIIIa–XIIIc). A mixture of an appropriate compound **XII** and 1-adamantanol taken in 3-fold excess was heated in 5 ml of trifluoroacetic acid at 70°C for 4 h. The solvent was distilled off, and the reaction mixture was subjected to column chromatography [eluent hexane–ethyl acetate, 2:1 (**XIIIa, XIIIb**), 3:1 (**XIIIc**) by volume].

Methyl 2-(1-adamantyl)-3-[1-(4-chlorophenyl)-2,5-dioxotetrahydro-1*H*-pyrrol-3-ylidene]propanoate (XIIIa) was obtained from 0.20 g (0.6 mmol) of compound **XIIa** and 0.27 g (1.8 mmol) of 1-adamantanol. Yield 0.045 g (17%), mp 174–175°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.52–1.82 m (12H, Ad), 2.04 br.s (3H, Ad), 2.92 d (1H, CH, *J* 11 Hz), 3.39 d (1H, CH_2, *J* 19 Hz), 3.48 d (1H, CH_2, *J* 19 Hz), 3.73 s (3H, OCH_3), 7.17 d (1H, =CH, *J* 11 Hz), 7.33 d (2H, C_6H_4, *J* 8 Hz), 7.46 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 67.23; H 6.03; N 3.23. $C_{24}H_{26}ClNO_4$. Calculated, %: C 67.36; H 6.12; N 3.27.

Ethyl 2-(1-adamantyl)-3-[1-(3-tolyl)-2,5-dioxotetrahydro-1*H*-pyrrol-3-ylidene]propanoate (XIIIb) was obtained from 0.20 g (0.63 mmol) of compound **XIIb** and 0.29 g (1.9 mmol) of 1-adamantanol. Yield of ester **XIIIb** 0.04 g (15%), mp 133–134°C. IR spectrum, cm^{-1}: 1030, 1180, 1320, 1380, 1460, 1490, 1680, 1720 v.s, 2910 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, CH_3, *J* 7 Hz), 1.60–1.80 m (12H, Ad), 2.04 br.s (3H, Ad), 2.41 s (3H, CH_3), 2.91 d (1H, CH, *J* 11 Hz), 3.37 d (1H, CH_2, *J* 19 Hz), 3.51 d (1H, CH_2, *J* 19 Hz), 4.19 q (2H, OCH_2, *J* 7 Hz), 7.16 d (1H, =CH, *J* 11 Hz), 7.19–7.40 m (4H, C_6H_4). Found, %: C 73.93; H 7.41; N 3.07. $C_{26}H_{31}NO_4$. Calculated, %: C 74.08; H 7.41; N 3.32.

Ethyl 2-(1-adamantyl)-3-[1-(2,4,6-trimethylphenyl)-2,5-dioxotetrahydro-1*H*-pyrrol-3-ylidene]-propanoate (XIIIc) was obtained from 0.20 g (0.58 mmol) of compound **XIIc** and 0.27 g (1.8 mmol) of 1-adamantanol. Yield 0.055 g (21%), mp 149–151°C. IR spectrum, cm^{-1}: 1030, 1180, 1310, 1380, 1460, 1490, 1680, 1720 v.s, 2910 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, CH_3, *J* 7 Hz), 1.61–1.82 m (12H, Ad), 2.04 br.s (3H, Ad), 2.08 s (3H, CH_3), 2.11 s (3H, CH_3), 2.32 s (3H, CH_3), 2.92 d (1H, CH, *J* 11 Hz), 3.41 d (1H, CH_2, *J* 19 Hz), 3.50 d (1H, CH_2, *J* 19 Hz), 4.22 q (2H, OCH_2, *J* 7 Hz), 6.99 s (2H, C_6H_2), 7.12 d (1H, =CH, *J* 11 Hz). Found, %: C 74.87; H 7.85; N 2.86. $C_{28}H_{35}NO_4$. Calculated, %: C 74.80; H 7.85; N 3.12.

Esters of substituted 2-acetyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic acids (**XIVa** and **XIVb**). A mixture of an appropriate compound I and the same weight amount of acetic anhydride in anhydrous toluene was heated at 110°C for 4 h. The solvent was distilled off in a vacuum, the residue was recrystallized from ethanol.

Ethyl 2-acetyl-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (XIVa) was obtained from 1 g (3.5 mmol) of compound **Ia** and 1 g of acetic anhydride in 20 ml of toluene. Yield of ester **XIVa** 1.02 g (89%), mp 181–183°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_3, *J* 7 Hz), 2.49 s (3H, CH_3), 4.41–4.49 m (2H, OCH_2), 4.90 d (1H, CH, *J* 11 Hz), 5.87 d (1H, CH, *J* 11 Hz), 7.24–7.47 m (5H, C_6H_5). Found, %: C 58.16; H 4.71; N 12.69. $C_{16}H_{15}N_3O_5$. Calculated, %: C 58.36; H 4.59; N 12.76.

Ethyl 2-acetyl-6,8-dioxo-7-(4-chlorophenyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylateat (XIVb) was obtained from 0.54 g (1.7 mmol) of compound **Ib** and 0.5 g of acetic anhydride in 10 ml of toluene. Yield 0.52 g (89%), mp 224–225°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_3, *J* 7 Hz), 2.49 s (3H, CH_3), 4.42–4.50 m (2H, OCH_2), 4.90 d (1H, CH, *J* 11 Hz), 5.87 d (1H, CH, *J* 11 Hz), 7.31 d (2H, C_6H_4, *J* 8 Hz), 7.47 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 52.71; H 3.65; N 11.51. $C_{16}H_{14}ClN_3O_5$. Calculated, %: C 52.83; H 3.88; N 11.56.

Ethyl 2-benzoyl-6,8-dioxo-7-ethyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (XIVc). To a solution of 0.50 g (2.1 mmol) of compound **Io** in 5 ml of DMF and 0.5 ml of triethylamine cooled with ice was added a solution of 0.3 g (2.1 mmol) of benzoyl chloride in 3 ml of DMF. The reaction mixture was stirred at room temperature for 12 h, then poured in water, the precipitate was filtered off and recrystallized from ethanol. Yield 0.24 g (33%), mp 156–157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 t (3H, CH_3, *J* 7 Hz), 1.39 t (3H, CH_3, *J* 7 Hz), 3.63 q (2H, NCH_2, *J* 7 Hz), 4.41 q (2H, OCH_2, *J* 7 Hz), 4.73 d (1H, CH, *J* 10 Hz), 5.98 d (1H, CH, *J* 10 Hz), 7.46 t (2H, C_6H_5, *J* 8 Hz), 7.55 t (1H, C_6H_5, *J* 8 Hz), 7.98 d (2H, C_6H_5, *J* 8 Hz). Found, %: C 59.41; H 4.87; N 12.14. $C_{17}H_{17}N_3O_5$. Calculated, %: C 59.47; H 4.99; N 12.24.

Ethyl 2-(1-adamantylcarbonyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (XIVd). A solution of 1.5 g (5.2 mmol) of compound **Ia** and 1.4 g (7 mmol) of adamantanecarbonyl chloride in 50 ml of anhydrous toluene was heated at 110°C for 10 h. The solution was evaporated to a volume of 20 ml, cooled, the separated precipitate was filtered off and recrystallized from a mixture ethanol–acetone. Yield of ester **XIVd** 2.15 g (93%), mp 234°C. UV spectrum (dichloroethane), λ_{max}, nm (log ε): 287 (3.45). IR spectrum, cm^{-1}: 1020, 1150, 1280 s, 1370 s, 1450, 1500, 1730 v.s, 2910 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 t (3H, CH_3, *J* 7 Hz), 1.77 br.s (6H, Ad), 2.02–2.22 m (9H, Ad), 4.43 q (2H, OCH_2, *J* 7 Hz), 4.75 d (1H, CH, *J* 10 Hz), 5.92 d (1H, CH, *J* 10 Hz), 7.22–7.50 m (5H, C_6H_5). Found, %: C 66.67; H 6.12; N 9.37. $C_{25}H_{27}N_3O_5$. Calculated, %: C 66.81; H 6.06; N 9.35.

Ethyl 2-(1-adamantylcarbonyl)-6,8-dioxo-7-cyclohexyl-2,3,7-triazabicyclo[3.3.0]-oct-3-ene-4-carboxylate (XIVe). A solution of 1.5 g (5.1 mmol) of compound **Id** and 1.4 g (7 mmol) of adamantanecarbonyl chloride in 25 ml of anhydrous toluene was heated at 110°C for 7 h. The solution was evaporated to a volume of 15 ml, cooled, the separated precipitate was filtered off and recrystallized from ethanol. Yield 2.2 g (94%), mp 209°C. UV spectrum (dichloroethane), λ_{max}, nm (log e): 287 (3.39). IR spectrum, cm^{-1}: 1020, 1160, 1280 s, 1360 s, 1460, 1570, 1720 v.s, 2910 C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–1.31 m (3H, Ad), 1.42 t (3H, CH_3, *J* 7 Hz), 1.50–1.88 m (12H, Ad), 2.00–2.20 m (10H, C_6H_{11}), 3.97–4.04 m (1H, C_6H_{11}), 4.43 q (2H, OCH_2, *J* 7 Hz), 4.52 d (1H, CH, *J* 11 Hz), 5.65 d (1H, CH, *J* 11 Hz). Found, %: C 65.73; H 7.31; N 9.25. $C_{25}H_{33}N_3O_5$. Calculated, %: C 65.87; H 7.25; N 9.22.

Esters of substituted 1-acetyl-6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylic acids (XVa–XVc). A mixture of 0.5 g of compound **XII** and 1 ml of acetyl chloride in 20 ml of anhydrous dichloromethane was heated at 40°C for 6 h. The solvent and excess acyl chloride were distilled off, and the residue was crystallized from ethanol.

Methyl 1-acetyl-7-(4-methyl-3-chlorophenyl)-6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (XVa) was obtained from 0.50 g (1.5 mmol) of compound **XIId**. Yield 0.51 g (91%), mp 167–168°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (3H, CH_3), 2.44 s (3H, CH_3), 2.95 d (1H, CH_2, *J* 19 Hz), 3.31 d (1H, CH_2, *J* 19 Hz), 3.42 d (1H, CH_2, *J* 19 Hz), 3.81 d (1H, CH_2, *J* 19 Hz), 3.94 s (3H, OCH_3), 7.15–7.37 s (3H, C_6H_3). Found, %: C 54.01; H 4.19; N 11.03. $C_{17}H_{16}ClN_3O_5$. Calculated, %: C 54.05; H 4.27; N 11.12.

Methyl 1-acetyl-6,8-dioxo-7-(4-chlorophenyl)-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (XVb) was obtained from 0.50 g (1.6 mmol) of compound

XIIa. Yield 0.49 g (87%), mp 179–181°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, CH_3), 2.95 d (1H, CH_2, *J* 19 Hz), 3.32 d (1H, CH_2, *J* 19 Hz), 3.42 d (1H, CH_2, *J* 19 Hz), 3.82 d (1H, CH_2, *J* 19 Hz), 3.95 s (3H, OCH_3), 7.32 d (2H, C_6H_4, *J* 8 Hz), 7.47 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 52.70; H 3.85; N 11.41. $C_{16}H_{14}ClN_3O_5$. Calculated, %: C 52.83; H 3.88; N 11.55.

Ethyl 1-acetyl-6,8-dioxo-7-(4-ethoxyphenyl)-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (XVc) was obtained from 0.50 g (1.5 mmol) of compound **XIIf**. Yield 0.41 g (74%), mp 143–144°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 t (3H, CH_3, *J* 7 Hz), 1.44 t (3H, CH_3, *J* 7 Hz), 2.44 s (3H, CH_3), 2.94 d (1H, CH_2, *J* 19 Hz), 3.31 d (1H, CH_2, *J* 19 Hz), 3.41 d (1H, CH_2, *J* 19 Hz), 3.82 d (1H, CH_2, *J* 19 Hz), 4.07 q (2H, OCH_2, *J* 7 Hz), 4.40 q (2H, OCH_2, *J* 7 Hz), 6.98 d (2H, C_6H_4, *J* 8 Hz), 7.24 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 58.84; H 5.43; N 10.69. $C_{19}H_{21}N_3O_6$. Calculated, %: C 58.91; H 5.46; N 10.85.

Ethyl 7-(3-methoxyphenyl)-6,8-dioxo-1-trifluoroacetyl-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (XVd). A mixture of 0.50 g (1.5 mmol) of compound **XIIg** and 1 ml of trifluoroacetic anhydride in 15 ml of anhydrous dichloromethane was heated at 40°C for 8 h. The solvent and excess anhydride were distilled off, the residue was crystallized from methanol. Yield of ester **XVd** 0.46 g (72%), mp 109–110°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 t (3H, CH_3, *J* 7 Hz), 3.05 d (1H, CH_2, *J* 19 Hz), 3.40 d (1H, CH_2, *J* 19 Hz), 3.43 d (1H, CH_2, *J* 19 Hz), 3.84 s (3H, OCH_3), 3.89 d (1H, CH_2, *J* 19 Hz), 4.41 q (2H, OCH_2, *J* 7 Hz), 6.88 d (1H, C_6H_4, *J* 2 Hz), 6.91 d (1H, C_6H_4, *J* 8 Hz), 7.01 d.d (1H, C_6H_4, *J* 8 θ 2 Hz), 7.42 t (1H, C_6H_4, *J* 8 Hz). Found, %: C 50.47; H 3.73; N 9.69. $C_{18}H_{16}F_3N_3O_6$. Calculated, %: C 50.59; H 3.77; N 9.83.

Methyl 1-(1-adamantylcarbonyl)-7-(4-bromophenyl)-6,8-dioxo-1,2,7-triazaspiro[4.4]-non-2-ene-3-carboxylate (XVe). A solution of 0.20 g (0.55 mmol) of compound **XIIe** and 0.13 g (0.8 mmol) of adamantanecarbonyl chloride in 8 ml of anhydrous toluene was heated at 110°C for 7 h. The solvent was evaporated at reduced pressure, the residue was subjected to preparative column chromatography (eluent hexane–ethyl acetate, 2:1 by volume). Yield 0.15 g (51%), mp 178–179°C. IR spectrum, cm^{-1}: 910, 1020, 1070, 1110, 1140, 1260, 1290, 1320, 1390, 1450, 1490, 1590, 1650, 1720 v.s, 2850, 2910 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.76 br.s (6H, Ad), 2.01–2.10 m (9H, Ad), 2.92 d (1H, CH_2, *J* 18 Hz), 3.18 d (1H, CH_2, *J* 18 Hz), 3.34 d (1H, CH_2, *J* 18 Hz), 3.66 d (1H, CH_2, *J* 18 Hz), 3.94 s (3H, OCH_3), 7.26 d (2H, C_6H_4, *J* 8 Hz), 7.63 d (2H, C_6H_4, *J* 8 Hz). Found, %: C 56.87; H 4.74; N 7.67. $C_{25}H_{26}BrN_3O_5$. Calculated, %: C 56.83; H 4.96; N 7.95.

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