ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 7, pp. 1014–1026. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.I. Kas'yan, I.N. Tarabara, Ya.S. Bondarenko, L.K. Svyatenko, A.V. Bondarenko, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 7, pp. 1020–1032.

Reactions of 4-Amino-4-azatricyclo[5.2.1.$0^{2,6\text{-}endo}$]dec-8-ene-3,5-dione with Dicarboxylic Acid Anhydrides

L. I. Kas'yan, I. N. Tarabara, Ya. S. Bondarenko, L. K. Svyatenko, and A. V. Bondarenko

Dnepropetrovsk National University, per. Nauchnyi 13, Dnepropetrovsk, 49050 Ukraine

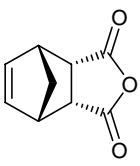
Received September 28, 2006

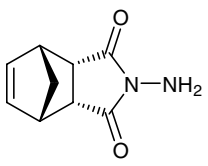
Abstract—Reactions of 4-amino-4-azatricyclo[5.2.1.$0^{2,6\text{-}endo}$]dec-8-ene-3,5-dione (hydrazinolysis product of endic anhydride) with succinic, maleic, *cis*-cyclohexane-1,2-dicarboxylic, endic, phthalic, and 1,8-naphthalic anhydrides were studied. Procedures for the preparation of the corresponding hydrazido acids and bis-imides were proposed. Their reactions with peroxyformic acid, depending on the substrate nature, led to the formation of both epoxy hydrazido acids and epoxy imides. The unsaturated adducts reacted with *p*-nitrophenyl azide to give the corresponding triazole derivatives.

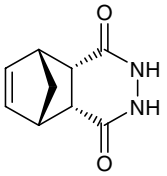
DOI: 10.1134/S1070428007070135

Organic hydrazine derivatives have found wide application in medicine as compounds exhibiting antituberculous, anticancer, psychotherapeutic, and other kinds of biological activity [1]. Some dicarboxylic acid hydrazides, in particular those derived from succinic, maleic, and phthalic acids, were found to possess bacteriostatic, antiphlogistic, analgetic, anticonvulsant, antiarrhythmic, hypertensive, and antiviral activity [2]. Compounds of this group are also characterized by pronounced antiaggregation effect [3] and hepatoprotective properties [4], and they induce liver cytochrome P-450 system [5].

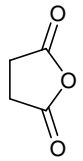
Products of hydrazine reactions with alicyclic acids, specifically with bicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboxylic (endic) acid, have been studied to a lesser extent. We previously [6] demonstrated that hydrazide **II** obtained by condensation of endic anhydride (**I**) with hydrazine hydrate can be converted into various organic compounds via reactions with a number of electrophilic reagents, such as arenesulfonyl chlorides, benzoyl chlorides, aromatic isocyanates, isothiocyanates, and oxiranes. The structure of hydrazide **II** was proved by the X-ray diffraction data [6], which ruled out alternative structure **IIa**. Reactions of compound **II** with dicarboxylic acid anhydrides were almost not studied previously; therefore, the goal of the present study was to fill up this gap.

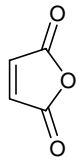

I

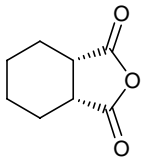

II

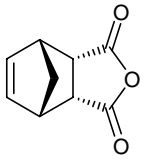

IIa

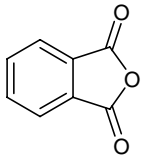
As reagents we used succinic, maleic, *cis*-cyclohexane-1,2-dicarboxylic, endic, phthalic, and 1,8-naphthalic anhydrides **IIIa**–**IIIf**.

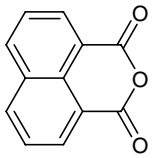

IIIa


IIIb


IIIc

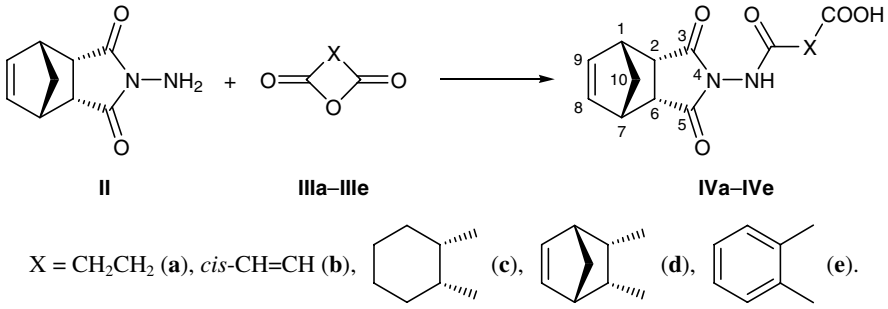

IIId


IIIe


IIIf

Reactions of hydrazide **II** with dicarboxylic acid anhydrides were carried out in anhydrous benzene, ethyl acetate, and chloroform. Following one of the procedures proposed for reactions of endic anhydride with various amines [7], we succeeded in obtaining hydrazido acids **IVd** and **IVe** in 80 and 76% yield, respectively (Scheme 1). The second procedure [8] implies reaction of equimolar amounts of hydrazide **II** and the corresponding anhydride on heating for a short time in ethyl acetate; here, the yields of **IVa**, **IVb**, and **IVe** were 53, 88, and 78%, respectively. The maximal

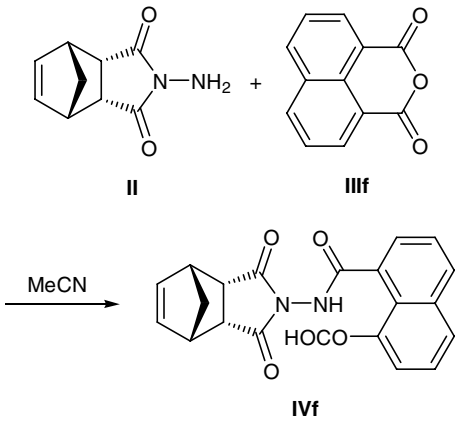
Scheme 1.



yields of **IVa**–**IVe** were obtained in the reactions of equimolar amounts of hydrazide **II** and anhydrides **III** in anhydrous chloroform. The reactions in benzene required the longest time (TLC), while the products formed in ethyl acetate required additional purification. The use of chloroform as solvent ensured considerably shorter reaction time and easier isolation procedure (unreacted initial compounds are removed by washing the product with the solvent).

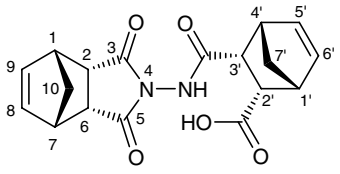
However, none of the above procedures turned out to be suitable for the synthesis of acid **IVf** from 1,8-naphthalic anhydride (**IIIf**). A probable reason is poor solubility of the reagent in the solvents used. Therefore, the reaction of **IIIf** with hydrazide **II** was carried out in acetonitrile, but the yield of target product **IVf** was only 12% (Scheme 2).

Scheme 2.



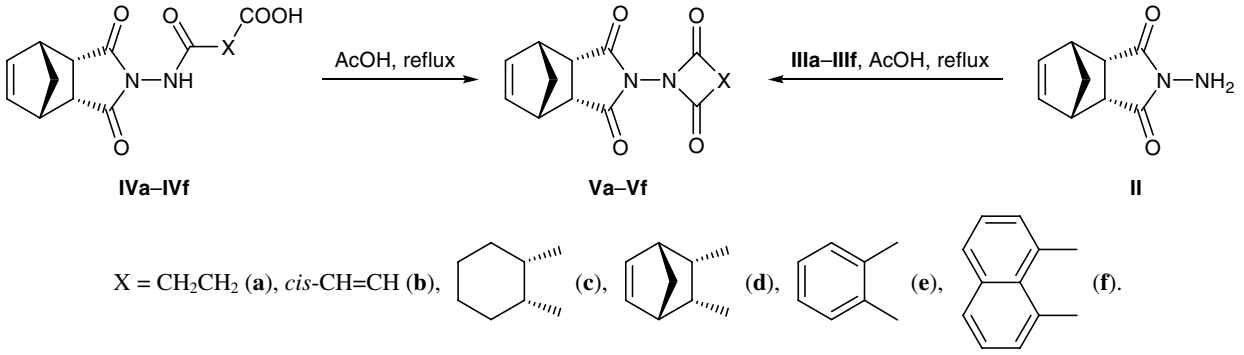
The IR spectra of acids **IVa**–**IVf** contained absorption bands due to imide carbonyl groups in the regions 1807–1760 and 1755–1735 cm^{-1}. The amide groups gave rise to absorption bands at 3320–3210, 1685–1625 (amide I), 1550–1525 (amide II), and 1270–1215 cm^{-1} (amide III), respectively [9]. The ^{1}H NMR spectra of compounds **IVb** and **IVe** were more informative from the viewpoint of structure assignment. Due to molecular symmetry, protons on C^8/C^9, C^1/C^7, and C^2/C^6 in the bicycloheptane skeleton resonated at δ 6.06/6.07, 3.44/3.46, and 3.28/3.35 ppm, respectively; the *syn*- and *anti*-10-H protons of the methylene bridge gave a single signal at δ 1.55 (**IVb**) and 1.56 ppm (**IVe**). Signals from protons in the exocyclic olefinic fragment in molecule **IVb** appeared at δ 6.48 and 6.14 ppm. The OH and NH signals were located at 10.79 and 10.90 ppm (**IVb**) and 6.25 and 7.72 ppm (**IVe**), respectively.

The ^{1}H NMR spectrum of compound **IVd** is more complex. Apart from signals belonging to the carboxy (OH, δ 11.52 ppm) and amide groups (NH, 6.10 ppm), the spectrum contained signals from protons in both bicycloheptene fragments, which appeared separately due to asymmetric structure of one of these fragments (amido acid). The 1-H and 7-H protons (δ 3.56 and 3.59 ppm), as well as protons of the methylene bridge (*syn*-10-H and *anti*-10-H; δ 1.58 and 1.53 ppm, respectively, ^2J = 8.7 Hz) in the imide fragment were nonequivalent. The other bicycloheptene fragment in molecule **IVd** was characterized by the following signals, δ, ppm: 6.22 (5′-H), 5.82 (6′-H), 3.29 (1′-H), 3.06 (4′-H), 3.10 (2′-H), 2.92 (3′-H), 1.31 and 1.22 (7-H, ^2J = 8.1 Hz).



Using thin-layer chromatography, we compared on a qualitative level the reactivity of anhydrides **IIIa**–**IIIe** toward 4-amino-4-azatricyclo[5.2.1.0$^{2,6\text{-}endo}$]dec-8-ene-3,5-dione (**II**) in chloroform. Samples of the reaction mixtures were withdrawn in increasing intervals (2, 5, 10, 30, and 60 min), and the plates were eluted with propan-2-ol–diethyl ether (1 : 10). The reaction

Scheme 3.



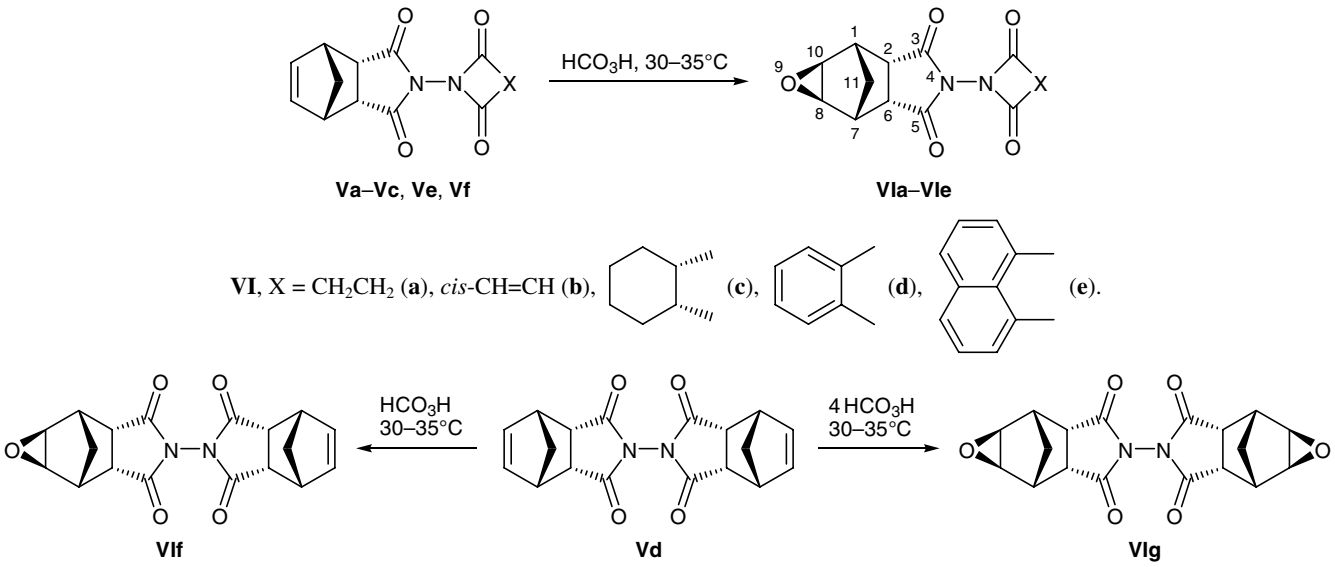
time increased in the series: **IVb** < **IVd** ≈ **IVc** < **IVe** < **IVa**; it was 10 h, 20 min, and 6 h in the synthesis of compounds **IVa**, **IVb**, and **IVd**, respectively.

Amido acids **IVa**–**IVf** were then converted into the corresponding bis-imides **Va**–**Vf** by heating in boiling glacial acetic acid (Scheme 3). Compounds **Va**–**Vf** were also synthesized directly from hydrazide **II** and the corresponding anhydride under analogous conditions. Bis-imides **Va** and **Vb** were obtained previously [10] just following the latter procedure. Hedaya and Hinmann [11] reported on successful preparation of imide **Vd** by heating 2 equiv of endic anhydride with hydrazine hydrate in alcohol. Bis-imides **Vc** and **Vd** were also isolated on attempted recrystallization of compounds **IVc** and **IVd** from propan-2-ol. Sample of bis-imides prepared by different procedures had identical melting points and IR spectra which contained absorption bands corresponding to the strained norbornene fragment at 3090–3075 ($\nu_{=C-H}$) and 745–715 cm^{-1} ($\delta_{=C-H}$) [12], as well as imide carbonyl absorption bands in the region 1820–1710 cm^{-1} [9]. Unlike amido acids **IV**, the ^1H NMR spectra of bis-imides **Vb**–**Ve** lacked signals assignable to carboxy and amide groups (OH, NH); in addition, the 1-H and 7-H signals appeared in a weaker field ($\Delta\delta$ = 0.22–0.28 ppm).

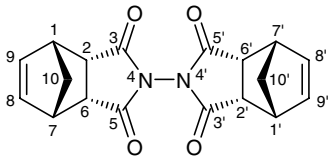
The presence of a strained double C=C bond in molecules of compounds **IV** and **V** makes them promising as subjects for studying their further transformations with participation of the unsaturated fragment. In particular, it was interesting to examine their reactions with peroxy acids and azides. It is known that many epoxy derivatives exhibit a broad spectrum of biological activity [13], and development of optimal procedures for their preparation is related to estimation of structural specificity of substrates and oxidant properties [14].

Bis-imides **Va**–**Vc**, **Ve**, and **Vf** were subjected to oxidation with peroxyformic acid which was previously shown to act as an effective epoxidizing agent toward cage-like imides [15]. Peroxyformic acid was

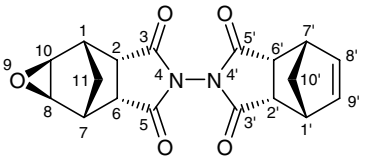
Scheme 4.



Calculated and experimental chemical shifts of protons in the bicyclic fragments of compounds **Vd** and **VIf**



Vd



VIf

Proton	Calculated chemical shifts δ, ppm		Experimental chemical shifts δ, ppm	
	Vd	**VIf**	**Vd**	**VIf**
1-H	3.36	2.98	3.56	3.57
2-H	3.14	3.00	3.27	2.95
6-H	3.11	2.97	3.27	2.95
7-H	3.34	2.96	3.55	3.52
8-H	6.96	3.35	6.04	3.16
9-H (10-H)	6.99	3.32	6.04	3.10
syn-10-H (*syn*-11-H)	1.86	1.94	1.56	1.38
anti-10-H (*anti*-11-H)	1.45	0.93	1.51	1.06
1′	3.36	3.38	3.56	3.57
2′	3.14	3.17	3.27	3.29
6′	3.11	3.20	3.27	3.29
7′	3.34	3.40	3.55	3.52
8′	6.96	7.03	6.04	6.08
9′	6.99	7.02	6.04	6.08
syn-10′-H	1.86	1.89	1.56	1.55
anti-10′-H	1.45	1.49	1.51	1.51

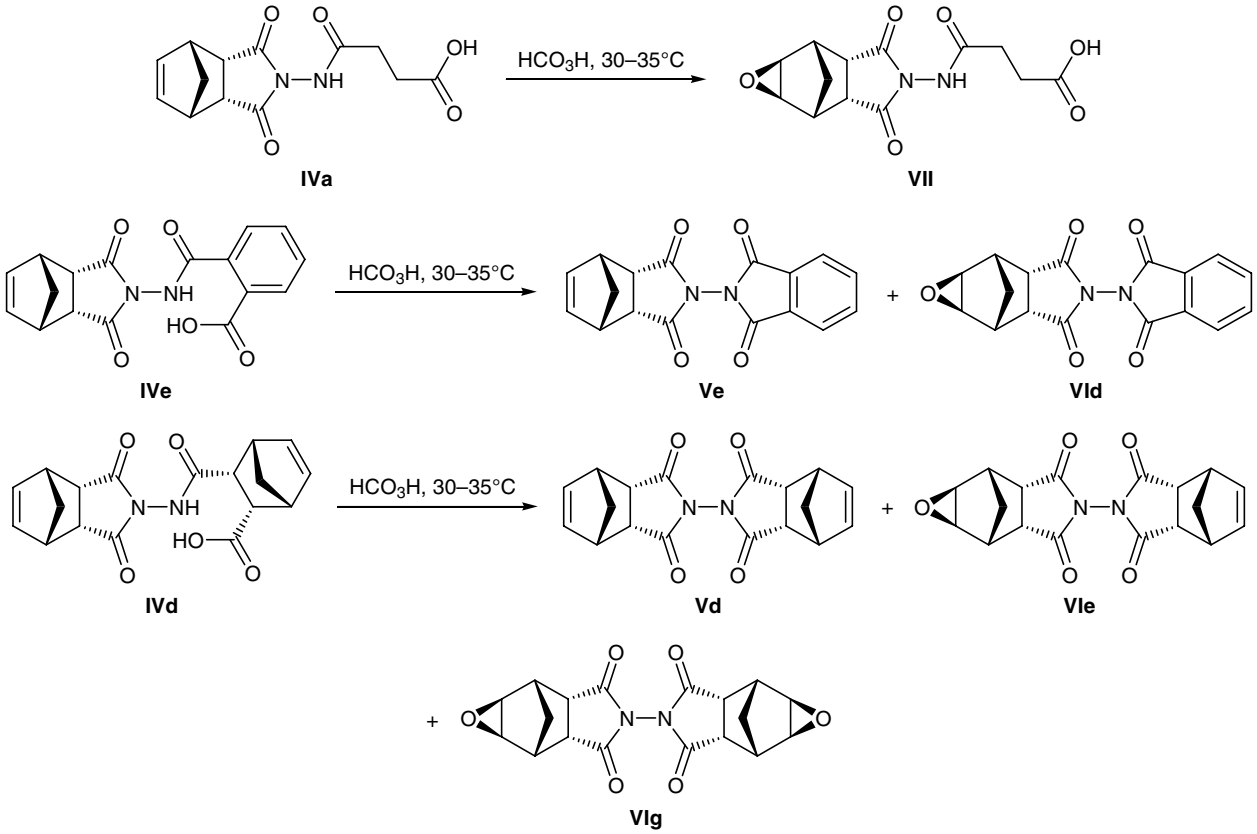
generated *in situ* from 98% formic acid and 50% hydrogen peroxide; no other solvent was added, and the reactions were carried out at 30–35°C under TLC control. In most cases, the reaction was complete in 2–4 h, and the only products were the corresponding epoxy bis-imides **VIa**–**VIe** (Scheme 4). Using different oxidant-to-substrate molar ratios in the reaction with bis-imide **Vd** having two equivalent strained double bonds we succeeded in isolating both mono- and di-epoxy derivatives **VIf** and **VIg**.

The oxidation of bis-imide **Vb** in which the double bonds are nonequivalent gave the corresponding mono epoxy derivative **VIb** only at the strained double bond in the bicycloheptene fragment, while the double bond in the maleimide moiety remained intact. The latter failed to undergo epoxidation with hydrogen peroxide in alkaline medium [16]. In the reaction of bis-imide **Vb** with equimolar amounts of potassium hydroxide and 50% hydrogen peroxide in alcohol, only hydrolysis products of imide **Vb** were isolated instead of oxidation products.

The structure of epoxy derivatives was confirmed by IR and ^{1}H NMR spectroscopy. Compounds **VIa**–**VIg** displayed in the IR spectra absorption bands typical of the imide fragments and bands at 865–855 cm^{-1} due to stretching vibrations of oxirane C–O bonds [13]. The ^{1}H NMR spectra of epoxides **VIb**, **VId**, **VIf**, and **VIg**, in contrast to their unsaturated precursors, contained signals at δ 3.12–3.20 ppm from protons in the three-membered ring, and the *anti*-11-H signal was displaced upfield (δ 1.01–1.12 ppm) due to magnetically anisotropic effect of the oxirane ring.

We calculated the chemical shifts of protons in molecules **Vd** and **VIf** for the gas phase in terms of the Hartree–Fock theory using the continuous set of gauge transformations method and standard 6-311++G(3*d*,2*p*) basis set [HF/CSGT/6-311++G(3*d*,2*p*)] [17]. The structures were optimized by the MP2/6-311G* method. The calculated values together with the experimental chemical shifts are given in table. The results of calculations strongly facilitated signal assignment in the ^{1}H NMR spectra and showed equivalence

Scheme 5.



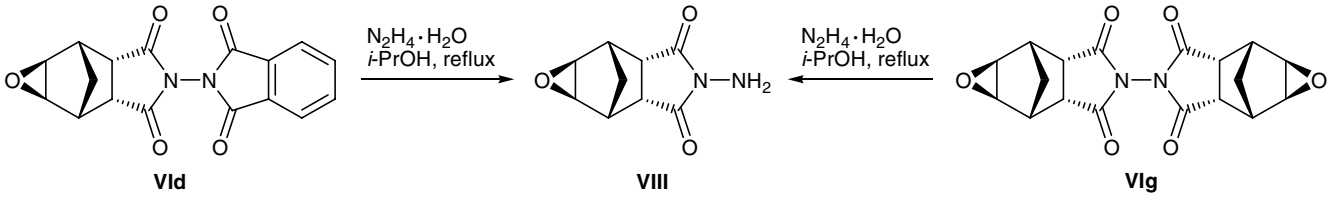
of protons in both cage-like fragments in molecule **Vd**. The chemical shifts of protons in molecule **Vd** decrease in the following series: 8-H, 9-H > 1-H, 7-H > 2-H, 6-H > *syn*-10-H > *anti*-10-H. The same series is retained for the unsaturated bicycloheptene fragment in monoepoxide **VIf**, while resonance of protons in the epoxy fragment is characterized by the series 8-H, 10-H > 1-H, 7-H ≈ 2-H, 6-H > *syn*-11-H > *anti*-11-H. As follows from the ^{1}H NMR data, molecule of bis-epoxide **VIg** is symmetric (like initial bis-imide **Vd**).

We also tried to oxidize hydrazido acids **IVa** and **IVe** with peroxyformic acid. From compound **IVa** we obtained epoxide **VII** (Scheme 5) whose structure was confirmed by the IR and ^{1}H NMR data. The oxidation of **IVe** with 2 equiv of peroxyformic acid (reaction time 24 h) gave imide **Ve** and its epoxy derivative **VId**; also, the initial compound was partially recovered from the reaction mixture, the ratio **IVe**:**Ve**:**VId** being 1.0:2.2:8.0 according to the ^{1}H NMR data. Under analogous conditions, the reaction with hydrazido acid **IVd** resulted in the formation of bis-imide **Vd**, its monoepoxy derivative **VIf**, and bis-epoxide **VIg** at a ratio of 1:10:40 (^{1}H NMR data). Using compound **IVd** as an example, we examined the effect of the reactant ratio on the composition of oxidation products. At an equimolar reactant ratio, the products were compounds **Vd**, **VIf**, and **VIg** at a ratio of 1.0:4.0:0.25. In the reaction of **IVd** with 4 equiv of HCO_3H we obtained bis-epoxy derivative **VIg** as the major product (72%), and the yields of compounds **Vd** and **VIf** were 2 and 8%, respectively (^{1}H NMR data).

We presumed that formic acid acts as dehydrating agent facilitating closure of imide ring and that the imides thus formed are oxidized with peroxyformic acid to the corresponding epoxy derivatives. In fact, when a mixture of acid **IVe** and 98% formic acid was stirred for 2 days in the absence of hydrogen peroxide, 23.2% of bis-imide **Ve** was formed. Heating of that mixture at 70–80°C resulted in almost complete transformation of **IVe** into bis-imide **Ve**.

The oxidation of hydrazide **II** with peroxyformic acid was accompanied by tarring, presumably due to the presence in molecule **II** of a primary amino group which is known to readily undergo oxidation and subsequent decomposition. Our attempt to effect epoxidation of compound **II** in the presence of *p*-toluenesulfonic acid (i.e., of the corresponding ammonium salt) was also unsuccessful. Therefore, we synthesized

Scheme 6.

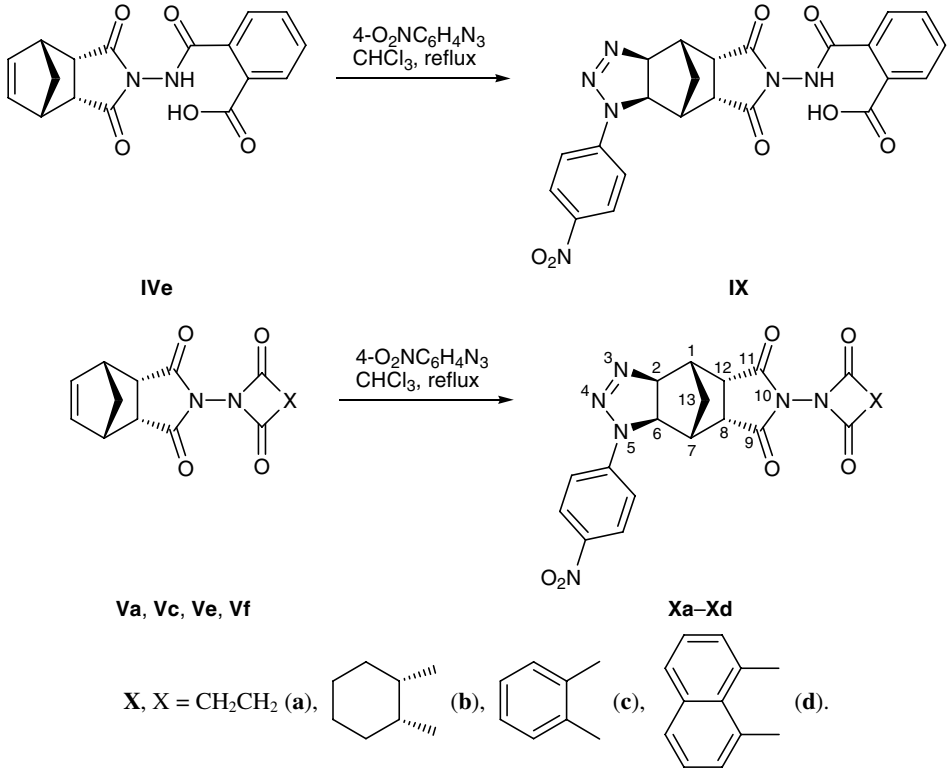


epoxy derivative of **II** by an indirect method. For this purpose, epoxy bis-imide **VId** was treated with 1.5 equiv of 80% aqueous hydrazine hydrate in boiling isopropyl alcohol. The yield of epoxy hydrazide **VIII** was 43% (Scheme 6). Better results were obtained using symmetric bis-epoxide **VIg** as initial compound; in this case, the yield of **VIII** was 67%, and the product was purer. Compound **VIII** showed in the IR spectrum absorption bands due to stretching vibrations of the imide carbonyl groups (1780–1690 cm^{-1}), N–H bonds in the primary amino group (3335 and 3280 cm^{-1} [9]), and oxirane C–O bonds (a strong band at 865 cm^{-1} [12]). Protons on C^{8} and C^{10} appeared in the ^{1}H NMR spectrum of **VIII** at δ 2.98 ppm, i.e., in the region typical of most epoxynorbornanes [18], and the amino group gave rise to a signal at δ 4.91 ppm.

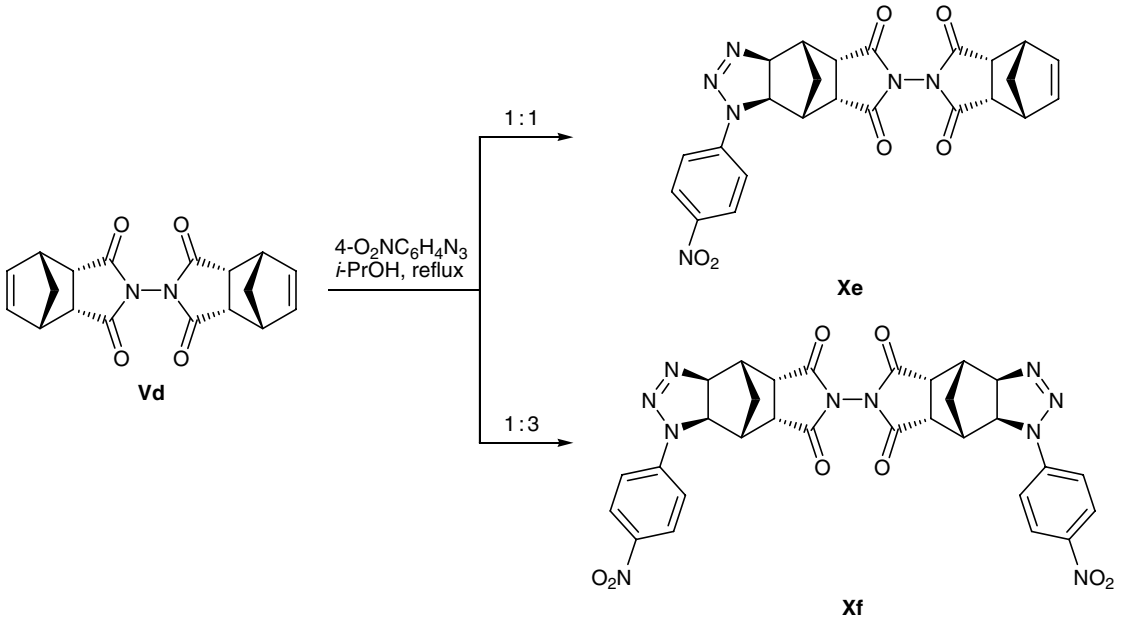
We also examined the behavior of unsaturated cage-like imides in dipolar [3+2]-cycloaddition to *p*-nitrophenyl azide. Both hydrazido acid **IVe** and bis-imides **Va**, **Vc**, **Ve**, and **Vf** were brought into reaction with *p*-nitrophenyl azide in boiling chloroform. As a result, the corresponding dihydro-1,2,3-triazole derivatives **IX** and **Xa**–**Xd** were isolated (Scheme 7). Insofar as bis-imide **Vd** is poorly soluble in chloroform, its reaction with *p*-nitrophenyl azide was carried out in boiling isopropyl alcohol. Depending on the reactant ratio, mono- and bis-triazolo derivatives **Xe** and **Xf** were obtained (Scheme 8).

The double C=C bonds in molecule **Vb** are nonequivalent. It is known [19] that the double bond in maleimide derivatives is also capable of reacting with aromatic azides according to the [3+2]-cycloaddition pattern. In the reaction of equimolar amounts of *p*-nitrophenylazide and bis-imide **Vb** in chloroform we isolated dihydrotriazole derivative **Xg** as the only product (Scheme 9); these data indicate higher reac-

Scheme 7.



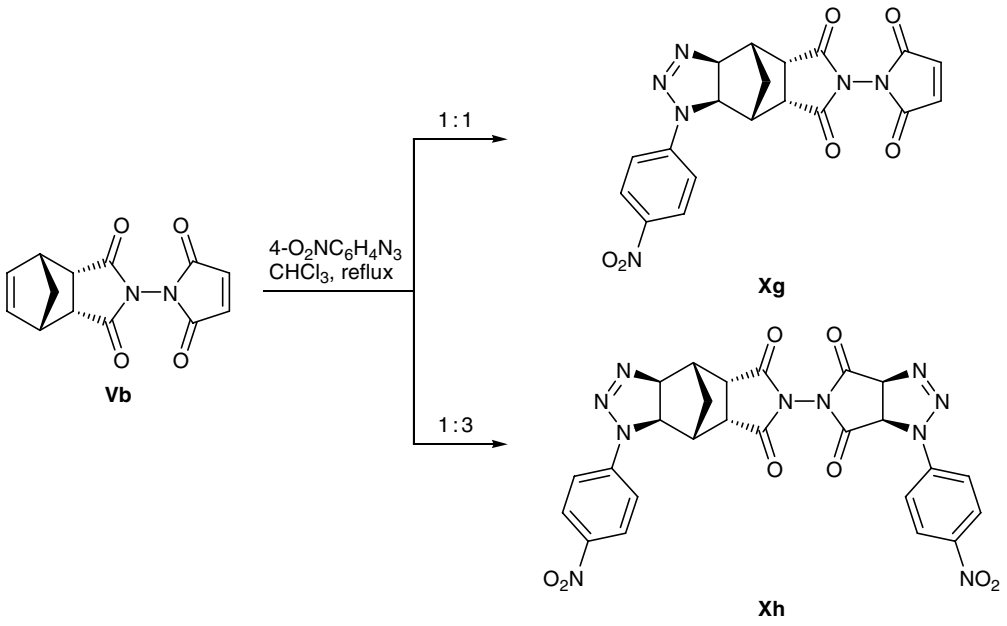
Scheme 8.



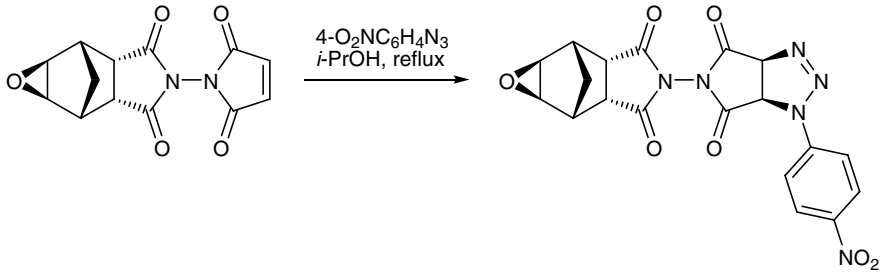
tivity of the strained C=C bond in the norbronene fragment. In the presence of 3 equiv of *p*-nitrophenylazide, the product was bis-triazole **Xh** resulting from azide addition at both unsaturated fragments in molecle **Vb**. Davis and Rondestvedt [20] showed that addition of azides to maleimides could produce both dihydrotriazole and aziridine derivatives, depending on the solvent. However, in the reaction of epoxy bis-imide **VIb** with *p*-nitrophenyl azide in boiling isopropyl alcohol we isolated only triazole derivative **XI** (Scheme 10).

In the IR spectra of compounds **IX**–**XI** we observed absorption bands arising from vibrations of the skeletal bonds, nitro group (1530–1515, 1350–1325 cm^{-1}), and N=N and aromatic C=C bonds (1610–1600 cm^{-1}) [9, 21]. Insofar as compounds **IX**, **Xc**, **Xe**–**Xh**, and **XI** contain unsymmetrically substituted dihydrotriazole fragments, their ^1H NMR spectra differ from the spectra of the corresponding epoxy derivatives and show considerable nonequivalence of protons in the tetracyclic skeleton (2-H/6-H, 1-H/7-H,

Scheme 9.



Scheme 10.



VIb **XI**

8-H/12-H). The largest difference in chemical shifts is observed for the 2-H and 6-H protons which resonate at δ 4.76–4.99 and 3.88–4.12 ppm, respectively (^3J = 8.7–9.4 Hz) [21, 22]. In the spectra of **IX**, **Xc**, and **Xe**–**Xh**, signal from one proton of the methylene bridge (*syn*-13-H) is slightly displaced downfield (δ 1.66–1.76 ppm) relative to the corresponding signal in the spectra of initial imides (δ 1.56–1.63 ppm), while the *anti*-13-H proton resonates in a stronger field (δ 1.14–1.34 ppm).

EXPERIMENTAL

The IR spectra were measured in KBr on UR-20 and Paragon 500 FT-IR spectrometers. The ^{1}H NMR spectra were recorded on Varian VXR-300 (300 MHz) and Varian Unity (200 MHz) spectrometers from solutions in DMSO-d_6 using HMDS or TMS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates (eluent isopropyl alcohol; development with iodine vapor). The elemental compositions were determined on a Carlo Erba analyzer.

4-Amino-4-azatricyclo[5.2.1.0$^{2,6\text{-}endo}$]dec-8-ene-3,5-dione (**II**) was prepared by reaction of 10.3 g (0.062 mol) of endic anhydride (**I**) with 6.1 ml (0.062 mol) of 80% aqueous hydrazine hydrate according to the procedure described in [23]. Yield 91.4%, mp 146–147°C; published data [23]: mp 145–146°C.

Imidocarbamoylcarboxylic acids IVa–IVe (*general procedure*). *a*. A mixture of 3.56 g (20 mmol) of compound **II** and 20 mmol of the corresponding dicarboxylic acid anhydride in 10 ml of benzene was stirred until the reaction was complete (TLC). The precipitate was filtered off, washed with benzene on a filter, dried in air, and subjected to additional treatment. This procedure was used to synthesize compounds **IVd** and **IVe**.

b. A mixture of 3.56 g (20 mmol) of compound **II** and 20 mmol of the corresponding dicarboxylic acid anhydride in 10 ml of ethyl acetate was heated until it became homogeneous. The mixture was left to stand until the reaction was complete (TLC), the solvent was removed under reduced pressure, and the residue was purified by recrystallization. In such a way, compounds **IVa** and **IVe** were obtained.

c. Compound **II**, 3.56 g (20 mmol), was dissolved in 10 ml of chloroform, 20 mmol of the corresponding dicarboxylic acid anhydride was added under stirring, and the mixture was stirred until the reaction was complete (TLC). The precipitate was filtered off, washed with chloroform on a filter, dried in air, and subjected to additional treatment. Following this procedure, compounds **IVa**–**IVe** were obtained.

4-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo-[5.2.1.0^{2,6}]dec-8-en-4-ylamino]-4-oxobutanoic acid (IVa). Yield 53 (*b*), 74% (*c*), mp 185–186°C (from propan-2-ol), R_f 0.58. IR spectrum, ν, cm^{-1}: 3250, 3215, 1790, 1740, 1720, 1625, 1530, 1250, 745. Found, %: N 10.10. $C_{13}H_{14}N_2O_5$. Calculated, %: N 10.07.

(*Z*)-4-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo-[5.2.1.0^{2,6}]dec-8-en-4-ylamino]-4-oxobut-2-enoic (IVb). Yield 88 (*b*) (oily substance), 76% (*c*), mp 128–130°C, R_f 0.69. IR spectrum, ν, cm^{-1}: 3515, 3320, 3080, 1807, 1755, 1715, 1665, 1530, 1255, 740, 725. ^{1}H NMR spectrum, δ, ppm: 10.79 s (1H, COOH), 6.48 d (1H, HC=, ^3J = 12.2 Hz), 6.25 s (1H, NH), 6.14 d (HC=), 6.06 m (2H, 8-H, 9-H), 3.44 m (2H, 1-H, 7-H), 3.28 m (2H, 2-H, 6-H), 1.55 d (2H, *syn*-10-H, *anti*-10-H). Found, %: H 10.25. $C_{13}H_{12}N_2O_5$. Calculated, %: N 10.14.

(1*S*,2*R*)-2-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-ylcarbamoyl]cyclohexanecarboxylic acid (IVc). Yield 69% (*c*), mp 159–160°C, R_f 0.82. IR spectrum, ν, cm^{-1}: 3340, 3220, 3085, 1760, 1740, 1715, 1660, 1535, 1270, 740. Found, %: N 8.27. $C_{17}H_{20}N_2O_5$. Calculated, %: N 8.43.

(1*S*,2*S*,3*R*,4*S*)-3-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-ylcarbamoyl]bicyclo-

[2.2.1]hept-5-ene-2-carboxylic acid (IVd). Yield 80 (*a*), 94% (*c*), mp 179–180°C (decomp.), R_f 0.46. IR spectrum, ν, cm^{-1}: 3510, 3210, 3085, 1800, 1745, 1725, 1650, 1550, 1215, 730. ^1H NMR spectrum, δ, ppm: 11.52 s (1H, COOH), 6.22 d.d (1H, 5′-H, $^3J_{5',6'}$ = 5.1, $^3J_{5',4'}$ = 2.5 Hz), 6.10 s (1H, NH), 6.06 m (2H, 8-H, 9-H), 5.82 d.d (1H, 6′-H, $^3J_{6',1'}$ = 2.5), 3.59 d.d (1H, 1-H), 3.56 d.d (1H, 7-H), 3.38 m (2H, 2-H, 6-H), 3.29 d.d (1H, 1′-H), 3.10 m (1H, 2′-H), 3.06 d.d (1H, 4′-H), 2.92 m (1H, 3′-H), 1.58 d (1H, *syn*-10-H, ^2J = 8.7 Hz), 1.53 d (1H, *anti*-10-H), 1.31 d (1H, *syn*-7′-H, ^2J = 8.1 Hz), 1.22 d (1H, *anti*-7′-H). Found, %: N 8.13. $C_{18}H_{18}N_2O_5$. Calculated, %: N 8.18.

2-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo-[5.2.1.$0^{2,6}$]dec-8-en-4-ylcarbamoyl]benzoic acid (IVe). Yield 76 (*a*), 78 (*b*), 84% (*c*), mp 160–161°C (from propan-2-ol), R_f 0.62. IR spectrum, ν, cm^{-1}: 3360, 3250, 3080, 1780, 1735, 1715, 1655, 1605, 1525, 1225, 735. ^1H NMR spectrum, δ, ppm: 10.90 s (1H, COOH), 7.50–7.76 m (4H, H_{arom}), 7.72 s (1H, NH), 6.07 m (2H, 8-H, 9-H), 3.46 m (2H, 1-H, 7-H), 3.35 m (2H, 2-H, 6-H), 1.56 d (2H, *syn*-10-H, *anti*-10-H). Found, %: N 8.61. $C_{17}H_{14}N_2O_5$. Calculated, %: N 8.59.

8-[(1*R*,2*R*,6*S*,7*R*)-(3,5-Dioxo-4-azatricyclo-[5.2.1.$0^{2,6}$]dec-8-en-4-ylcarbamoyl]naphthalene-1-carboxylic acid (IVf) was synthesized by stirring a mixture of 0.50 g (0.28 mmol) of compound **II** and 0.56 g (0.28 mmol) of 1,8-naphthalic anhydride in 15 ml of acetonitrile for 5 days. Yield 12%, mp 177–179°C, R_f 0.53. IR spectrum, ν, cm^{-1}: 3350, 3240, 3080, 1780, 1755, 1725, 1685, 1620, 1595, 1530, 1235, 735. Found, %: N 7.53. $C_{21}H_{16}N_2O_5$. Calculated, %: N 7.44.

Bis-imides Va–Vf (*general procedure*)**.** *a*. A mixture of 20 mmol of compound **IV** was heated in 15 ml of glacial acetic acid under reflux until the reaction was complete (TLC). The solvent was removed under reduced pressure, the residue was treated with 5–7 ml of cold water, and the precipitate was filtered off, washed on a filter with a small amount of water, dried, and subjected to further treatment.

b. A mixture of 1.78 g (10 mmol) of compound **II** and 10 mmol of dicarboxylic acid anhydride **IIIa–IIIf** in 20 ml of glacial acetic acid was heated under reflux until the reaction was complete (TLC). The solvent was removed under reduced pressure, the residue was treated with 8–10 ml of cold water, and the precipitate was filtered off, washed on a filter with a small amount of water, dried, and subjected to further treatment.

c. A solution of 20 mmol of compound **IVc** or **IVd** in 15–20 ml of ethanol was heated for 5–7 min under reflux and was then allowed to slowly cool down. The precipitate of bis-imide **Vc** or **Vd** was filtered off, washed on a filter with 3–5 ml of ethanol, and dried in air. Compounds **Vc** or **Vd** obtained in such a way required no additional purification.

(1*R*,2*R*,6*S*,7*R*)-4-(2,5-Dioxopyrrolidin-1-yl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (Va). Yield 80 (*a*), 77% (*b*), mp 205–206°C (from propan-2-ol), R_f 0.68; published data [10]: yield 72%, mp 227–229°C. IR spectrum, ν, cm^{-1}: 3080, 1815, 1755, 1735, 1270, 718. Found, %: N 10.62. $C_{13}H_{12}N_2O_4$. Calculated, %: N 10.76.

(1*R*,2*R*,6*S*,7*R*)-4-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (Vb). Yield 82 (*a*), 78% (*b*), mp 202–203°C (from propan-2-ol), R_f 0.77; published data [10]: yield 78%, mp 217–219°C. IR spectrum, ν, cm^{-1}: 3075, 1805, 1790, 1745, 1715, 1280, 720. ^1H NMR spectrum, δ, ppm: 7.35 d (1H, HC=, ^3J = 6.8 Hz), 7.32 d (HC=), 6.13 m (2H, 8-H, 9-H), 3.66 m (1H, 1-H), 3.65 m (1H, 7-H), 3.37 m (1H, 2-H), 3.36 m (1H, 6-H), 1.62 d (1H, *syn*-10-H, ^2J = 8.7 Hz), 1.57 d (1H, *anti*-10-H). Found, %: N 10.90. $C_{13}H_{10}N_2O_4$. Calculated, %: N 10.85.

(1*R*,2*R*,6*S*,7*R*)-4-[(3a*R*,7a*S*)-1,3-Dioxooctahydro-2*H*-isoindol-2-yl]-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (Vc). Yield 78 (*a*), 65 (*b*), 83% (*c*), mp 168–171°C (from ethanol), R_f 0.70. IR spectrum, ν, cm^{-1}: 3090, 1805, 1760, 1730, 1270, 735. ^1H NMR spectrum, δ, ppm: 6.12 m (2H, 8-H, 9-H), 3.65 m (1H, 1-H), 3.63 m (1H, 7-H), 3.31 m (2H, 2-H, 6-H), 1.61 d (1H, *syn*-10-H, ^2J = 8.7 Hz), 1.57 d (1H, *anti*-10-H). Found, %: N 9.03. $C_{17}H_{18}N_2O_4$. Calculated, %: N 8.91.

(1*S*,2*R*,6*S*,7*S*)-4-[(1*R*,2*R*,6*S*,7*R*)-3,5-Dioxo-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl]-4-azatricyclo-[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (Vd). Yield 95 (*a*), 83 (*b*), 78% (*c*), mp 298–299°C (from ethanol), R_f 0.11; published data [11]: yield 68%, mp 283–285°C. IR spectrum, ν, cm^{-1}: 3080, 1805, 1745, 1715, 1255, 740, 720. ^1H NMR spectrum, δ, ppm: 6.04 m (4H, 8-H, 9-H, 8′-H, 9′-H), 3.56 m (2H, 1-H, 1′-H), 3.55 m (2H, 7-H, 7′-H), 3.27 m (4H, 2-H, 6-H, 2′-H, 6′-H), 1.56 d (2H, *syn*-10-H, *syn*-10′-H, ^2J = 9.4 Hz), 1.51 d (2H, *anti*-10-H, *anti*-10′-H). Found, %: N 8.72. $C_{18}H_{16}N_2O_4$. Calculated, %: N 8.64.

(1*R*,2*R*,6*S*,7*R*))-4-(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (Ve). Yield 85 (*a*), 77% (*b*), mp 191–192°C (from propan-2-ol), R_f 0.71. IR spectrum, ν, cm^{-1}: 3080,

1820, 1790, 1775, 1750, 1620, 1240, 715. ^{1}H NMR spectrum, δ, ppm: 7.95–8.06 m (4H, H_{arom}), 6.17 m (2H, 8-H, 9-H), 3.72 m (1H, 1-H), 3.71 m (1H, 7-H), 3.37 m (2H, 2-H, 6-H), 1.63 d (1H, *syn*-10-H, ^2J = 9.8 Hz), 1.58 d (1H, *anti*-10-H). Found, %: N 9.14. $C_{17}H_{12}N_2O_4$. Calculated, %: N 9.09.

2-[(1*R*,2*R*,6*S*,7*R*)-3,5-Dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl}-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-1,3-dione (Vf). Yield 82 (*a*), 82% (*b*), mp 225–227°C (from acetic acid), R_f 0.27. IR spectrum, ν, cm^{-1}: 3085, 1805, 1785, 1745, 1710, 1595, 1240, 745. Found, %: N 7.78. $C_{21}H_{14}N_2O_4$. Calculated, %: N 7.82.

Epoxy bis-imides VIa–VIg (*general procedure*). A mixture of 5 mmol of bis-imide **Va–Ve** and 0.58 ml (10 mmol) of 50% aqueous hydrogen peroxide in 10 ml of 98% formic acid was stirred at room temperature until the reaction was complete (TLC). Volatile products were removed under reduced pressure, the residue was treated with 1–2 ml of cold water, and the precipitate was off, washed on a filter with a small amount of cold water, dried in air, and subjected to additional purification.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-(2,5-Dioxopyrrolidin-1-yl)-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIa). Yield 77%, mp 225–228°C (sublimes; from ethyl acetate), R_f 0.76. IR spectrum, ν, cm^{-1}: 3030, 1760, 1750, 1730, 1260, 862. Found, %: N 10.05. $C_{13}H_{12}N_2O_5$. Calculated, %: N 10.14.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIb). Yield 95%, mp 270–272°C (from propan-2-ol), R_f 0.54. IR spectrum, ν, cm^{-1}: 3035, 1810, 1755, 1740, 1275, 860. ^{1}H NMR spectrum, δ, ppm: 7.38 m (2H, HC=), 3.61 m (1H, 2-H), 3.60 m (1H, 6-H), 3.13 m (2H, 8-H, 10-H), 3.01 m (2H, 1-H, 7-H), 1.42 d (1H, *syn*-11-H, ^2J = 10.0 Hz), 1.11 d (1H, *anti*-11-H). Found, %: N 10.15. $C_{13}H_{10}N_2O_5$. Calculated, %: N 10.22.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-[(3a*R*,7a*S*)-1,3-Dioxooctahydro-2*H*-isoindol-2-yl]-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIc). Yield 77%, mp 211–212°C (from ethanol), R_f 0.87. IR spectrum, ν, cm^{-1}: 3030, 1810, 1755, 1720, 1280, 860. Found, %: N 8.54. $C_{17}H_{18}N_2O_5$. Calculated, %: N 8.48.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VId). Yield 83%, mp 214–215°C (from propan-2-ol), R_f 0.84. IR spectrum, ν, cm^{-1}: 1805, 1785, 1755, 1610, 1270, 865. ^{1}H NMR spectrum, δ, ppm: 7.97–8.10 m (4H, H_{arom}), 3.67 m (1H, 2-H), 3.65 m (1H, 6-H), 3.20 m (2H, 8-H, 10-H), 3.03 m (2H, 1-H, 7-H), 1.43 d (1H, *syn*-11-H, ^2J = 10.4 Hz), 1.12 d (1H, *anti*-11-H). Found, %: N 8.72. $C_{17}H_{12}N_2O_5$. Calculated, %: N 8.64.

2-{(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-(1,3-Dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-2-yl)}-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIe). Yield 76%, mp 279–281°C (from methanol). IR spectrum, ν, cm^{-1}: 3030, 1745, 1715, 1600, 1240, 860. Found, %: N 7.45. $C_{21}H_{14}N_2O_5$. Calculated, %: N 7.48.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-{(1*S*,2*R*,6*S*,7*S*)-3,5-Dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl}-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIf) was synthesized according to the general procedure from 0.50 g (0.15 mmol) of bis-imide **Vd** and 0.13 g (0.19 mmol) of 50% aqueous hydrogen peroxide. Yield 74%, mp 278–279°C (sublimes; from ethanol), R_f 0.49. IR spectrum, ν, cm^{-1}: 3080, 3030, 1780, 1755, 1280, 858, 720. ^{1}H NMR spectrum, δ, ppm: 6.11 m (2H, 8′-H, 9′-H), 3.55 m (4H, 2-H, 6-H, 2′-H, 6′-H), 3.12 m (1H, 8-H, ^3J = 3.4 Hz), 3.07 m (2H, 1-H, 7′-H), 3.05 m (1H, 10-H), 2.95 m (2H, 1′-H, 7-H), 1.58 d (1H, *syn*-10′-H, ^2J = 8.7 Hz), 1.52 d (1H, *anti*-10′-H), 1.38 d (1H, *syn*-11-H, ^2J = 8.1 Hz), 1.06 d (1H, *anti*-11-H). Found, %: N 8.25. $C_{18}H_{16}N_2O_5$. Calculated, %: N 8.23.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-{(1*R*,2*R*,6*S*,7*R*,8*S*,10*R*)-3,5-Dioxo-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undec-4-yl}-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIg) was synthesized from 1.64 g (5 mmol) of bis-imide **Vd** and 1.16 ml (20 mmol) of 50% aqueous hydrogen peroxide according to the general procedure. Yield 66%, mp 312–315°C (sublimes), R_f 0.60. IR spectrum, ν, cm^{-1}: 3025, 1805, 1775, 1745, 1715, 1280, 860, 855. ^{1}H NMR spectrum, δ, ppm: 3.57 m (4H, 2-H, 6-H, 2′-H, 6′-H), 3.16 m (4H, 8-H, $^3J_{8,10}$ = 3.4 Hz, 8′-H, $^3J_{8',10'}$ = 3.4 Hz), 3.10 m (2H, 10-H, 10′-H), 2.96 m (4H, 1-H, 7-H, 1′-H, 7′-H), 1.38 d (2H, *syn*-11-H, ^2J = 10.2 Hz, *syn*-11′-H, ^2J = 10.1 Hz), 1.07 d (2H, *anti*-11-H, *anti*-11′-H). Found, %: N 7.74. $C_{18}H_{16}N_2O_6$. Calculated, %: N 7.86.

4-{(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-(3,5-Dioxo-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undec-4-ylamino}-4-oxobutanoic acid (VII). Yield 72%, mp 218–220°C (from ethanol), R_f 0.89. IR spectrum, ν, cm^{-1}: 3350, 3240, 3020, 1790, 1740, 1710, 1690, 1620, 1440, 1280, 860. ^{1}H NMR spectrum, δ, ppm: 12.20 s (1H, COOH), 10.45 s (1H, NH), 3.35 m (2H, 2-H, 6-H), 3.06 m (2H, 8-H, 10-H), 2.91 m (2H, 1-H, 7-H), 1.38 d (1H, *syn*-

11-H, ^2J = 10.0 Hz), 1.05 d (1H, *anti*-11-H). Found, %: N 9.50. $C_{13}H_{14}N_2O_6$. Calculated, %: N 9.52.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-Amino-9-oxa-4-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane-3,5-dione (VIII). *a*. A mixture of 1.20 g (3.9 mmol) of epoxy bis-imide **VId** and 0.37 g (5.9 mmol) of 80% aqueous hydrazine hydrate in 10 ml of propan-2-ol was heated for 12 h under reflux. The mixture was cooled, and the precipitate was filtered off, dried in air, and recrystallized from propan-2-ol.

b. A mixture of 0.80 g (2.5 mmol) of epoxy bis-imide **VIg** and 0.24 g (3.8 mmol) of 80% aqueous hydrazine hydrate in 7 ml of propan-2-ol was heated for 12 h under reflux. The mixture was cooled, and the precipitate was filtered off, dried in air, and recrystallized from propan-2-ol. Yield 43 (*a*), 67% (*b*), mp 213–215°C, R_f 0.71. IR spectrum, ν, cm^{-1}: 3335, 3275, 3020, 1780, 1725, 1685, 1270, 865. ^{1}H NMR spectrum, δ, ppm: 4.91 s (2H, NH_2), 3.16 m (2H, 2-H, 6-H), 2.98 m (2H, 8-H, 10-H), 2.84 m (2H, 1-H, 7-H), 1.32 d (1H, *syn*-11-H, ^2J = 10.0 Hz), 1.01 d (1H, *anti*-11-H). Found, %: N 14.39. $C_9H_{10}N_2O_3$. Calculated, %: N 14.43.

2-{(1*S*,2*R*,6*S*,7*S*,8*S*,12*R*)-11-(4-Nitrophenyl)-3,5-dioxo-4,9,10,11-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]-tridec-9-en-4-ylcarbamoyl}benzoic acid (IX). A mixture of 0.50 g (1.5 mmol) of acid **VIe** and 0.37 g (2.3 mmol) of *p*-nitrophenyl azide in 10 ml of chloroform was heated under reflux until the reaction was complete (TLC). The solvent was removed under reduced pressure, and the residue was recrystallized from propan-2-ol. Yield 79%, mp 171–172°C (decomp.; from propan-2-ol). IR spectrum, ν, cm^{-1}: 3530, 3400, 1790, 1755, 1720, 1605, 1520, 1345, 1270, 860. ^{1}H NMR spectrum, δ, ppm: 13.50 s (1H, COOH), 8.32 s (1H, NH), 8.12 d (2H, H_{arom}), 7.98–8.06 m (4H, H_{arom}), 7.25 d (2H, H_{arom}), 4.89 d (1H, 2-H, $^3J_{2,6}$ = 9.4 Hz), 4.05 d (1H, 6-H), 3.70 m (2H, 8-H, 12-H), 3.27 m (1H, 1-H), 3.21 m (1H, 7-H), 1.76 d (1H, *syn*-13-H, ^2J = 10.0 Hz), 1.34 d (1H, *anti*-13-H). Found, %: N 17.18. $C_{23}H_{18}N_6O_7$. Calculated, %: N 17.14.

Dihydrotriazole derivatives Xa–Xd (*general procedure*). A mixture of 5 mmol of bis-imide **Va**, **Vc**, **Vd**, and **Vf** and 1.23 g (7.5 mmol) of *p*-nitrophenyl azide in 10 ml of chloroform was heated under reflux until the reaction was complete (TLC). The mixture was cooled, and the precipitate was filtered off, thoroughly washed with chloroform on a filter dried in air, and recrystallized from ethanol.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-(2,5-Dioxopyrrolidin-1-yl)-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-ene-9,11-dione (Xa). Yield 68%, mp 249–251°C (decomp.). IR spectrum, ν, cm^{-1}: 1798, 1755, 1610, 1528, 1342, 1260, 858. Found, %: N 19.91. $C_{19}H_{16}N_6O_6$. Calculated, %: N 19.80.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-[(3a*R*,7a*S*)-1,3-Dioxo-octahydro-2*H*-isoindol-2-yl]-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-ene-9,11-dione (Xb). Yield 77%, mp 189–190°C (decomp.). IR spectrum, ν, cm^{-1}: 1774, 1752, 1744, 1732, 1598, 1518, 1334, 1276, 848. Found, %: N 17.61. $C_{23}H_{22}N_6O_6$. Calculated, %: N 17.56.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-ene-9,11-dione (Xc). Yield 90%, mp 222–224°C. IR spectrum, ν, cm^{-1}: 1810, 1785, 1755, 1730, 1605, 1515, 1340, 1235, 856. ^{1}H NMR spectrum, δ, ppm: 8.29 d (2H, H_{arom}), 8.01–8.11 m (4H, H_{arom}), 7.32 d (2H, H_{arom}), 4.86 d (1H, 2-H, $^3J_{2,6}$ = 8.5 Hz), 4.02 d (1H, 6-H), 3.80 m (2H, 8-H, 12-H), 3.21 m (2H, 1-H, 7-H), 1.68 d (1H, *syn*-13-H, ^2J = 11.6 Hz), 1.17 d (1H, *anti*-13-H). Found, %: N 17.72. $C_{23}H_{16}N_6O_6$. Calculated, %: N 17.79.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-(1,3-Dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-2-yl)-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-ene-9,11-dione (Xd). Yield 75%, mp 247–248°C (decomp.). IR spectrum, ν, cm^{-1}: 1790, 1750, 1710, 1605, 1600, 1530, 1340, 1240, 855. Found, %: N 16.12. $C_{27}H_{18}N_6O_6$. Calculated, %: N 16.08.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-{(1*R*,2*R*,6*S*,7*R*)-3,5-Dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl}-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]-tridec-3-ene-9,11-dione (Xe). A mixture of 1.62 g (5.0 mmol) of bis-imide **Vd** and 0.82 g (5 mmol) of *p*-nitrophenyl azide in 20 ml of propan-2-ol was heated under reflux until the reaction was complete (TLC). The precipitate was filtered off, washed on a filter with a large amount of propan-2-ol, dried in air, and recrystallized from ethanol. Yield 74%, mp 264–266°C (decomp.). IR spectrum, ν, cm^{-1}: 3090, 1770, 1750, 1740, 1610, 1525, 1342, 1270, 855, 760. ^{1}H NMR spectrum, δ, ppm: 8.33 d (2H, H_{arom}), 7.30 d (2H, H_{arom}), 6.15 m (2H, 8′-H, 9′-H), 4.76 d (1H, 2-H, $^3J_{2,6}$ = 8.7 Hz), 3.88 d (1H, 6-H), 3.78 m (2H, 8-H, 12-H), 3.69 m (2H, 1′-H, 7′-H), 3.32 m (2H, 2′-H, 6′-H), 3.25 m (1H, 1-H), 3.16 m (1H, 7-H), 1.66 d (1H, *syn*-13-H, ^2J = 11.2 Hz), 1.61 d (1H, *syn*-10′-H, ^2J = 8.7 Hz), 1.57 d (1H, *anti*-10′-H), 1.14 d (1H, *anti*-13-H). Found, %: N 17.29. $C_{24}H_{20}N_6O_6$. Calculated, %: N 17.21.

(1*R*,2*R*,6*S*,7*R*,8*S*,12*R*)-10-{(1*S*,2*R*,6*S*,7*S*,8*S*,12*R*)-11-(4-Nitrophenyl)-3,5-dioxo-4,9,10,11-tetraazatetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]tridec-9-ene-4-yl}-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo-[5.5.1.$0^{2,6}$.$0^{8,12}$]tridec-3-ene-9,11-dione (Xf) was synthesized in a similar way from 1.62 g (5 mmol) of bis-imide **Vd** and 1.46 g (15 mmol) of *p*-nitrophenyl azide. Yield 31%, mp 259–260°C (decomp.). IR spectrum, ν, cm^{-1}: 1780, 1754, 1735, 1610, 1520, 1345, 1285, 860, 855. ^{1}H NMR spectrum, δ, ppm: 8.32 d (2H, H_{arom}), 8.09 d (2H, H_{arom}), 7.34 d (2H, H_{arom}), 7.24 d (2H, H_{arom}), 4.99 d (1H, 2′-H, $^3J_{2',6'}$ = 9.3 Hz), 4.88 d (1H, 2-H, $^3J_{2,6}$ = 8.7 Hz), 4.12 d (1H, 6′-H), 3.92 d (1H, 6-H), 3.78 m (4H, 8-H, 12-H, 8′-H, 12′-H), 3.31 m (2H, 1-H, 1′-H), 3.29 m (2H, 7-H, 7′-H), 1.66 d (2H, *syn*-13-H, ^2J = 11.2 Hz, *syn*-13′-H, ^2J = 11.2 Hz), 1.16 d (2H, *anti*-13-H, *anti*-13′-H). Found, %: N 21.52. $C_{30}H_{24}N_{10}O_8$. Calculated, %: N 21.46.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]tridec-3-ene-9,11-dione (Xg). A mixture of 0.40 g (1.6 mmol) of bis-imide **Vb** and 0.25 g (1.6 mmol) of *p*-nitrophenyl azide in 10 ml of chloroform was heated under reflux until the reaction was complete (TLC). The mixture was cooled, and the precipitate was filtered off, thoroughly washed with chloroform on a filter, dried in air, and recrystallized from chloroform. Yield 73%, mp 216–218°C. IR spectrum, ν, cm^{-1}: 1805, 1760, 1610, 1520, 1345, 1270, 860, 760. ^{1}H NMR spectrum, δ, ppm: 8.32 d (2H, H_{arom}), 7.43 m (2H, HC=), 7.33 d (2H, H_{arom}), 4.78 d (1H, 2-H, $^3J_{2,6}$ = 8.7 Hz), 3.94 d (1H, 6-H), 3.77 m (2H, 8-H, 12-H), 3.30 m (1H, 1-H), 3.20 m (1H, 7-H), 1.67 d (1H, *syn*-13-H, ^2J = 11.2 Hz), 1.17 d (1H, *anti*-13-H). Found, %: N 19.78. $C_{19}H_{14}N_6O_6$. Calculated, %: N 19.90.

(1*S*,2*S*,6*R*,7*S*,8*R*,12*S*)-10-{(3a*S*,6a*R*)-1-(4-Nitrophenyl)-4,6-dioxo-1,3a,4,5,6,6a-hexahydropyrrolo-[3,4-*d*][1,2,3]triazol-5-yl}-5-(4-nitrophenyl)-3,4,5,10-tetraazatetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]tridec-3-ene-9,11-dione (Xh) was synthesized in a similar way by heating a mixture of 0.40 g (1.6 mmol) of bis-imide **Vb** and 0.75 g (4.8 mmol) of *p*-nitrophenyl azide in 15 ml of chloroform under reflux. Yield 43%, mp 195–198°C. IR spectrum, ν, cm^{-1}: 1810, 1795, 1760, 1605, 1525, 1345, 870, 860. ^{1}H NMR spectrum, δ, ppm: 8.26 d (2H, H_{arom}), 7.37 d (2H, H_{arom}), 6.31 d (1H, 1′-H, $^3J_{1',5'}$ = 10.6 Hz), 5.71 d (1H, 5′-H), 3.62 m (2H, 2-H, 6-H), 3.14 m (2H, 8-H, 9-H), 3.02 m (2H, 1-H, 7-H), 1.42 d (1H, *syn*-10-H, ^2J = 10.0 Hz), 1.11 d (1H, *anti*-10-H). Found, %: N 23.90. $C_{25}H_{18}N_{10}O_8$. Calculated, %: N 23.88.

(1*S*,2*R*,6*S*,7*S*,8*S*,10*R*)-4-{(3a*S*,6a*R*)-1-(4-Nitrophenyl)-4,6-dioxo-1,3a,4,5,6,6a-hexahydropyrrolo-[3,4-*d*][1,2,3]triazol-5-yl}-9-oxa-4-azatetracyclo-[5.3.1.$0^{2,6}$.$0^{8,10}$]undecane-3,5-dione (XI) was synthesized in a similar way by heating a mixture of 0.50 g (1.8 mmol) of epoxy bis-imide **VIb** and 0.30 g (1.8 mmol) of *p*-nitrophenyl azide in 15 ml of propan-2-ol under reflux. Yield 24%, mp 196–199°C (decomp.). IR spectrum, ν cm^{-1}: 1785, 1760, 1610, 1530, 1350, 1325, 870, 860. ^{1}H NMR spectrum, δ, ppm: 8.32 d (2H, H_{arom}), 8.09 d (2H, H_{arom}), 7.34 d (2H, H_{arom}), 7.23 d (2H, H_{arom}), 6.28 d (1H, 1′-H, $^3J_{1',5'}$ = 10.6 Hz), 5.58 d (1H, 5′-H), 4.77 d (1H, 2-H, $^3J_{2,6}$ = 8.7 Hz), 3.93 d (1H, 6-H), 3.78 m (1H, 8-H), 3.66 m (1H, 12-H), 3.14 m (1H, 1-H), 2.59 m (1H, 7-H), 1.69 d (1H, *syn*-13-H, ^2J = 11.2 Hz), 1.18 d (1H, *anti*-13-H). Found, %: N 19.21. $C_{19}H_{14}N_6O_7$. Calculated, %: N 19.17.

REFERENCES

1. Overberger, C.G., Anselme, J.-P., and Lombardino, J.G., *Organic Compounds with Nitrogen–Nitrogen Bonds*, New York: Ronald, 1966; Shvaika, O., *Osnovi sintezu likars'kikh rechovin* (Principles of Synthesis of Medicines), Donets'k: Skhidnii Vidavnichii Dim, 2002.
2. Kolotova, N.V., Koz'minykh, E.N., Kolla, V.E., Syropyatov, B.Ya., Voronina, E.V., and Koz'minykh, V.O., *Khim.-Farm. Zh.*, 1999, no. 5, p. 22; Kolotova, N.V., Dolzhenko, A.V., Koz'minykh, V.O., Kotegov, V.P., and Godina, A.T., *Khim.-Farm. Zh.*, 1999, no. 9, 9; Dolzhenko. A.V., Kolotova, N.V., Koz'minykh, V.O., Syropyatov, B.Ya., Kotegov, V.P., Godina, A.T., and Rudakova, G.V., *Khim.-Farm. Zh.*, 2003, no. 4, p. 24; Dolzhenko, A.V., Kolotova, N.V., Koz'minykh, V.O., Syropyatov, B.Ya., Kotegov, V.P., Godina, A.T., and Rudakova, G.V., *Khim.-Farm. Zh.*, 2003, no. 1, p. 21; Dolzhenko, A.V., Koz'minykh, V.O., Kolotova, N.V., Burdi, N.E., Novoselova, G.N., and Syropyatov, B.Ya., *Khim.-Farm. Zh.*, 2003, no. 7, p. 7; Dolzhenko, A.V., Koz'minykh, V.O., Kolotova, N.V., Syropyatov, B.Ya., and Novoselova, G.N., *Khim.-Farm. Zh.*, 2003, no. 5, p. 10; Dolzhenko, A.V., Kolotova, N.V., Koz'minykh, V.O., and Syropyatov, B.Ya., *Khim.-Farm. Zh.*, 2002, no. 3, p. 17; Dolzhenko, A.V., Kolotova, N.V., Koz'minykh, V.O., Syropyatov, B.Ya., Kotegov, V.P., and Godina, A.T., *Khim.-Farm. Zh.*, 2002, no. 2, p. 6; Dolzhenko, A.V., Kolotova, N.V., Koz'minykh, V.O., Syropyatov, B.Ya., and Novoselova, G.N., *Khim.-Farm. Zh.*, 2002, no. 4, p. 11.
3. Krys'ko, A.A., Yatsyuk, D.I., Kabanov, V.M., Kabanova, T.A., Karaseva, T.L., and Andronati, S.A., *Khim.-Farm. Zh.*, 2003, no. 3, p. 38.

4. Sal'nikova, S.I., Il'ina, T.V., Zhuravlev, N.S., and Verdyan, A.I., *Khim.-Farm. Zh*., 1990, no. 5, p. 25.
5. Burdulene, D., Stumbryavichute, Z., Talaikite, Z., Lysenkova, E.M., and Drozdova, V.I., *Khim.-Farm. Zh*., 1995, no. 4, p. 11.
6. Kas'yan, L.I., Tarabara, I.N., Bondarenko, Ya.S., Shishkina, S.V., Shishkin, O.V., and Musatov, V.I., *Russ. J. Org. Chem*., 2005, vol. 41, p. 1122.
7. Kas'yan, A.O., Krishchik, O.V., Krasnovskaya, O.Yu., and Kas'yan, L.I., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1731; Kas'yan, L.I., Krishchik, O.V., Krasovskii, V.A., Okovityi, S.I., Tarabara, I.N., and Pal'chikov, V.A., *Vopr. Khim. Khim. Tekhnol*., 2004, no. 2, p. 35.
8. Kolotova, N.V., Dolzhenko, A.V., Kuz'minykh, V.O., Kotegov, V.P., and Godina, A.T., *Khim.-Farm. Zh*., 1999, no. 12, p. 9.
9. Nakanishi, K., *Infrared Absorption Spectroscopy. Practical*, San Francisco: Holden-Day, 1962; Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.
10. Augustin, M. and Reinemann, R., *Z. Chem*., 1973, vol. 13, p. 61.
11. Nedaya, E. and Ninmann, R.L., *J. Org. Chem*., 1966, vol. 31, p. 1317.
12. Zefirov, N.S. and Sokolov, V.I., *Usp. Khim*., 1967, vol. 36, p. 243.
13. Dryuk, V.G., Kartsev, V.G., and Voitsekhovskaya, M.A., *Oksirany – sintez i biologicheskaya aktivnost'* (Oxiranes: Synthesis and Biological Activity), Moscow: Bogorodskii Pechatnik, 1999.
14. Prilezhaeva, E.N., *Reaktsiya Prilezhaeva. Elektrofil'noe okislenie* (Prilezhaev Reaction. Electrophilic Oxidation), Moscow: Nauka, 1974.
15. Kas'yan, L.I., Krishchik, O.V., Umrykhina, L.K., and Kas'yan, A.O., *Visn. Dnipropetr. Univ., Khim*., 1998, no. 3, p. 87.
16. Haines, A.H., *Methods for the Oxidation of Organic Compounds. Akanes, Alkenes, Alkynes, and Arenes*, London: Academic, 1985.
17. Møller, C. and Plesset, M.S., *Phys. Rev*., 1934, vol. 46, p. 618; Helgaker, T., Jaszunski, M., and Ruud, K., *Chem. Rev*., 1999, vol. 99, p. 293; Keith, T.A. and Bader, R.F.W., *Chem. Phys. Lett*., 1993, vol. 210, no. 1, p. 223; Hehre, W.J., Ditchfield, R., and Pople, J.A., *J. Chem. Phys*., 1972, vol. 56, p. 2257.
18. Kas'yan, L.I., *Russ. J. Org. Chem*., 1999, vol. 35, p. 635.
19. L'abbe, G., *Chem. Rev*., 1969, vol. 69, p. 345.
20. Davis, S.J. and Rondestvedt, C.S., *Chem. Ind*., 1956, vol. 18, p. 845.
21. Kas'yan, L.I., Tarabara, I.N., Kas'yan, A.O., and Yarovoi, M.Yu., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1629; Tarabara, I.N., Kas'yan, A.O., Yarovoi, M.Yu., Shishkina, S.V., Shishkin, O.V., and Kas'yan, L.I., *Russ. J. Org. Chem*., 2004, vol. 40, p. 992.
22. Baraclough, D., Oakland, J.S., and Scheinmann, F., *J. Chem. Soc., Perkin Trans. 1*, 1972, p. 1500; Oakland, J.S. and Scheinmann, F., *J. Chem. Soc., Perkin Trans. 1*, 1973, p. 800.
23. Augustin, M. and Reinemann, R., *Z. Chem*., 1972, vol. 12, p. 101.