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Reactions of Bicyclo[2.2.1]hept-5-ene-2,3-dicarboximides with Aromatic Azides

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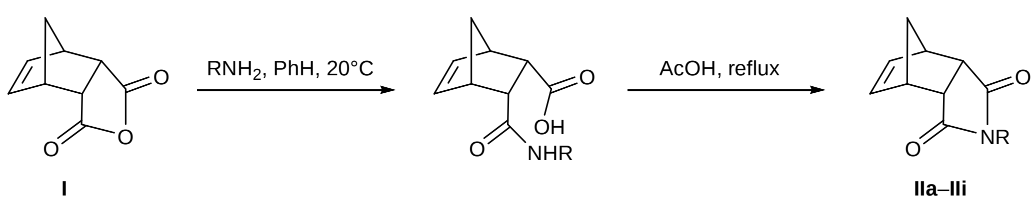
Abstract—Reactions of *N*-substituted bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximides with *o*- and *p*-nitrophenyl azides, as well as with *p*-nitrophenylsulfonyl azide and *p*-toluenesulfonyl azide, afforded the corresponding substituted dihydrotriazole (from aryl azides) and arylsulfonylaziridine derivatives (from sulfonyl azides). The *exo* orientation of the nitrogen-containing cyclic fragments (in keeping with the Alder rule) and *endo* orientation of the imide ring were confirmed by analysis of the IR and ^{1}H and ^{13}C NMR spectra. The molecular structure of one of the products was examined by X-ray analysis.

Norbornene and its derivatives occupy a specific place in organic chemistry. The presence of a rigid bicyclic skeleton gives rise to stereoisomers with fixed spatial orientation of substituents [1]. The double bond in substituted norbornenes exhibits specific properties arising from steric strain therein; it can readily be involved in reactions implying formation of cyclic transition states, in particular in 1,3-dipolar addition with azides [2, 3]. The mechanism of these reactions was established on the basis of kinetic data [4]. Using reactions of aryl azides with stereoisomeric bicyclo-[2.2.1]hept-5-ene-2,3-dicarboximides as examples [4], it was found that both electron-donor and electron-acceptor substituents in the azide molecules accelerate the reaction. This affect was interpreted in terms of variation in orbital donor–acceptor interactions between the dipolarophiles and 1,3-dipoles [4]. The reaction of phenyl azide with bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarbonitrile was also examined, and the products thus obtained were tested for anticarcinogenic activity [5].

Reactions of norbornene, endic anhydride, and the *exo* stereoisomer of the latter with phenylsulfonyl azide were reported to give phenylsulfonylaziridines; however, the stereochemical aspects of these reactions were doubtful [6], so that they require further confirmation. According to the data of [6, 7], the formation of aziridines from the corresponding dihydrotriazole intermediates is accompanied by change of the initial *exo* orientation of the nitrogen-containing fragment with respect to the bicyclic skeleton, which is known as the Alder *exo*-attack rule and is also typical of reactions of substituted norbornenes with peroxy acids, leading to oxirane ring fusion [8].

The goal of the present work was to study reactions of N-substituted bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic (endic) acid imides with aryl- and

Scheme 1.



II, R = H (**a**), *i*-Pr (**b**), *t*-Bu (**c**), $PhCH_2$ (**d**), *p*-MeC_6H_4 (**e**), *o*,*p*-$Me_2C_6H_3$ (**f**), *m*,*p*-$Cl_2C_6H_3$ (**g**), *p*-$O_2NC_6H_4$ (**h**), 2-pyridyl (**i**).

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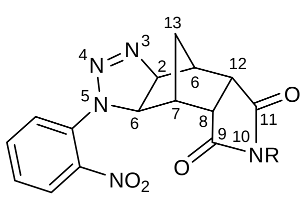
sulfonyl azides. The initial imides were synthesized by the known procedure including aminolysis of endic anhydride under mild conditions and subsequent dehydration of amido acids thus formed by heating in boiling glacial acetic acid (Scheme 1). Imides **IIa** and **IId**–**IIh** were described in [9]. The IR spectra of compounds **II** contained absorption bands belonging to asymmetric and symmetric stretching vibrations of the carbonyl groups at 1780–1730 and 1710–1680 cm^{-1} and bands from vibrations of the aromatic ring (in the spectra of *N*-aryl and *N*-benzyl derivatives); compound **IIa** showed in the spectrum a distinct band at 3157 cm^{-1} due to stretching vibrations of the NH group, and in the spectrum of imide **IIh** bands at 1520 and 1355 cm^{-1} were present due to stretching vibrations of the nitro group [10].

The reactions of imides **IIa**–**IIi** with *p*- and *o*-nitrophenyl azides were carried out in boiling chloroform with equimolar amounts of the reactants. The progress of reactions was monitored by TLC. The reactions took 7 to 15 h, the slowest reaction was that with imide **IIh** containing an electron-acceptor nitro group. From *o*-nitrophenyl azide and imides **IIa**–**IIe** and **IIi** we obtained dihydrotriazole derivatives **IIIa**–**IIIf**, while *p*-nitrophenyl azide gave rise to compounds **IVa**–**IVf**. The IR spectra of products **IIIa**–**IIIf** and **IVa**–**IVf** retained carbonyl absorption of the imide fragment (1765–1750 and 1720–1690 cm^{-1}) and absorption bands due to stretching vibrations of the nitro group (1530–1510 and 1360–1325 cm^{-1}). A medium-intensity band in the region 1610–1595 cm^{-1} (which was absent in the IR spectra of the initial imides) is likely to belong to stretching vibrations of the N=N bond in the triazole fragment [10, 11].

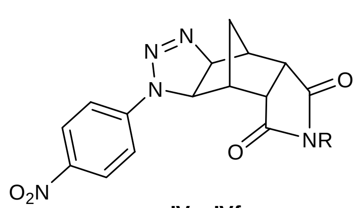
The ^{1}H NMR spectra of triazolonorbornenes **III** and **IV** reflect asymmetric structure of their molecules. Unlike initial imides, "twin" protons (2-H/6-H and 1-H/7-H) and in some cases 8-H and 12-H in **III** and **IV** are nonequivalent. The strongest differences in the chemical shifts were observed for protons in the triazole fragment (2-H and 6-H), whose signals are located at δ 3.8–4.2 and 4.5–5.0 ppm, respectively. These protons are coupled through a constant ^3J of 9.0–9.3 Hz. One proton at the methylene bridge (*anti*-13-H) resonates in a stronger field (δ 1.12–1.45 ppm), while the position of signal from the other proton is retained. The upfield shift of the signal from *anti*-13-H which is located above the triazole ring plane indicates that the reaction of imides **II** with aryl azides follows the Alder rule [1].

An analogous pattern was observed in the ^{13}C NMR spectra of compounds **IIIa**, **IVc**, **IVd**, and **IVf**. The signals therein were assigned using the Rubenstein–Nakashima technique. The chemical shifts of C^2 and C^6 are δ_C 56–57 and 83–84 ppm, respectively. The carbonyl carbon nuclei of the imide fragment give signals in the δ_C region 175–177 ppm. Comparison with the spectra of unsaturated imides [9] shows an upfield shift of signals from carbon nuclei belonging to the triazole fragment (C^2, C^6) and from protons of the methylene bridge (C^{13}).

The structure of compound **IIIa** was proved by the X-ray diffraction data (see table and figure). Compound **IIIa** crystallizes as a 1:1 solvate with a 1*H*-isoindol-1-one molecule. The pyrrole and triazole rings are planar within 0.03 and 0.02 Å, respectively.

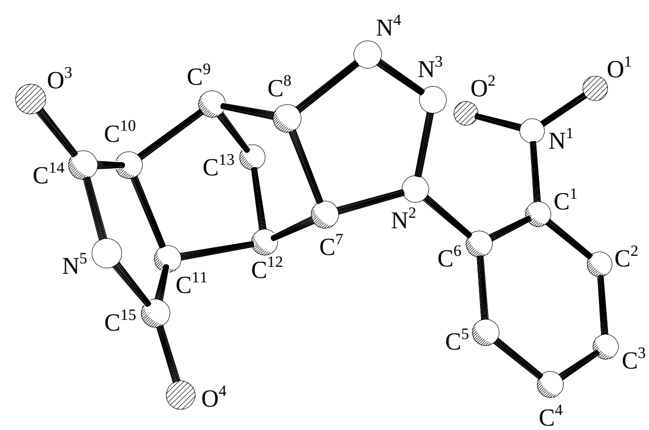


IIIa–IIIf



IVa–IVf

IIIa, **IVa**, R = H; **IIIb**, **IVb**, R = *i*-Pr; **IIIc**, R = *t*-Bu; **IIId**, R = $PhCH_2$; **IIIe**, **IVc**, R = *p*-MeC_6H_4; **IVd**, R = *m*,*p*-$Cl_2C_6H_3$; **IVe**, R = *p*-$O_2NC_6H_4$; **IIIf**, **IVf**, R = 2-pyridyl.



Molecular structure of 5-*o*-nitrophenyl-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (**IIIa**) according to the X-ray diffraction data.

Coordinates ($\times 10^4$) of non-hydrogen atoms and their equivalent isotropic thermal parameters ($E^2 \times 10^3$) in the structure of 5-*o*-nitrophenyl-3,4,5,10-tetraazatricyclo-[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (**IIIa**) as a solvate with 1*H*-isoindol-1-one molecule (S)

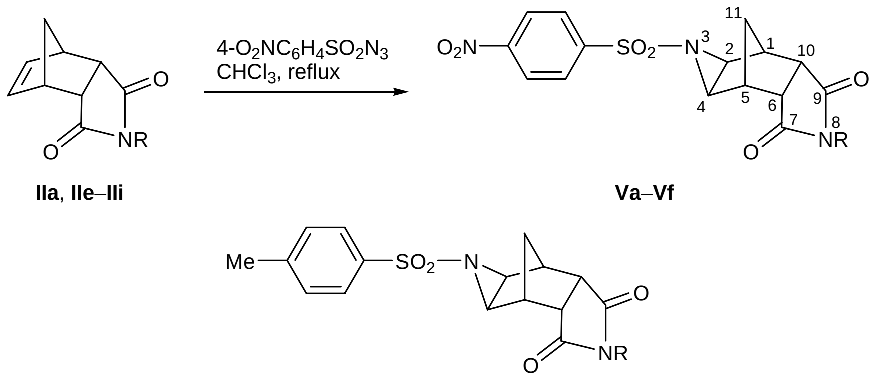
Atom	*x*	*y*	*z*	U_{eq}
O^1	1386(6)	3835(5)	4060(3)	106(2)
O^2	1815(5)	1930(4)	4216(3)	92(1)
O^3	180(5)	–1280(3)	9712(2)	71(1)
O^4	6091(5)	–202(3)	8627(2)	75(1)
N^1	2230(6)	2960(6)	4329(3)	70(1)
N^2	2876(5)	2034(3)	6374(3)	54(1)
N^3	1079(6)	2359(3)	6393(3)	61(1)
N^4	0(6)	1778(4)	7041(3)	64(1)
N^5	3133(5)	–607(3)	9359(3)	57(1)
C^1	3917(6)	3153(4)	4750(3)	50(1)
C^2	5232(7)	3800(4)	4144(3)	61(1)
C^3	6918(7)	3905(4)	4438(3)	59(1)
C^4	7281(7)	3380(4)	5353(4)	64(1)
C^5	5959(6)	2758(4)	5984(3)	53(1)
C^6	4249(6)	2629(3)	5702(3)	44(1)
C^7	3131(6)	1112(4)	7163(3)	45(1)
C^8	1121(6)	892(4)	7581(3)	53(1)
C^9	879(7)	–388(4)	7250(3)	57(1)
C^{10}	1890(6)	–1252(4)	7914(3)	55(1)
C^{11}	3905(7)	–969(4)	7579(3)	58(1)
C^{12}	3886(6)	–70(4)	6658(3)	51(1)
C^{13}	2190(6)	–450(4)	6199(3)	63(1)
C^{14}	1567(8)	–1080(4)	9092(4)	60(1)
C^{15}	4583(7)	–561(4)	8552(4)	55(1)
C^{1S}	2549(7)	4535(6)	9869(4)	84(2)
C^{2S}	1935(9)	3690(6)	10622(5)	112(2)
C^{3S}	1396(9)	4134(6)	11606(4)	99(2)
C^{4S}	1422(9)	5327(6)	11796(4)	99(2)
C^{5S}	2048(9)	6173(6)	11065(5)	105(2)
C^{6S}	2617(9)	5723(6)	10078(5)	97(2)
C^{7S}	3311(9)	6395(6)	9169(6)	105(2)
N^{1S}	3602(7)	5606(7)	8463(4)	108(2)
C^{8S}	3193(9)	4489(7)	8807(6)	107(2)
O^{1S}	3364(9)	3591(6)	8295(5)	187(2)

The O^3 atom slightly deviates from the pyrrole ring plane: the torsion angle $O^3C^{14}C^{10}C^{11}$ is –174.9(4)°. The nitro group is turned with respect to the benzene ring plane: the torsion angle $O^1N^1C^1N^2$ is –54.4(5)°, but the C^1–N^1 bond is not elongated: 1.452(6) Å against the standard value 1.468 Å [12]. The benzene and triazole ring planes form an angle of –28.9(5)° ($C^1C^6N^3N^3$) due to repulsion between the N^1 and N^3 atoms (the $N^1\cdots N^3$ distance is 2.75 Å which is shorter than the sum of the corresponding van der Waals radii, 3.00 Å [13]). The N^2–C^6 bond [1.409(5) Å] is longer than the standard C–N bond [1.371(16) Å], presumably due to electron-acceptor character of the nitrophenyl and triazole rings.

The torsion angles $H^8C^8C^7H^7$ and $H^{10}C^{10}C^{11}H^{11}$ are equal to –5°, indicating *cis*-junction of the bicycloheptane fragment with the triazole and pyrrole rings. Orientation of the five-membered rings with respect to the bicycloheptane fragment is determined by the transoid orientation of the H^{10}/H^{11} and H^7/H^8. Thus the triazole ring lies approximately in the plane formed by the C^7, C^8, C^{10}, and C^{11} atoms, while the pyrrole ring is almost orthogonal to that plane. This arrangement of the rings gives rise to shortened intramolecular contacts $H^8\cdots C^{14}$ 2.50, $H^7\cdots C^{15}$ 2.56, $H^{10}\cdots C^{13}$ 2.68, $H^{11}\cdots C^{13}$ 2.87, and $H^2\cdots H^{13\text{-}anti}$ 2.56 Å (2.66 Å). The molecule of 1*H*-isoindol-1-one is planar within 0.01 Å. Molecules **IIIa** in crystal are linked to dimers through intramolecular hydrogen bonds $N^5H\cdots O^4$ [$N^5H\cdots O^4$ 2.06 Å, $\angle N^5HO^4$ 168°).

Apart from aryl azides, we examined arylsulfonyl azides as reagents for addition at the strained double bond of norbornenedicarboximides. *p*-Nitrophenylsulfonyl and *p*-tolylsulfonyl azides were synthesized by the procedure described in [14]. Their reactions with imides **IIa** and **IIe**–**IIi** were performed in boiling chloroform using equimolar amounts of the reactants (Scheme 2). The reaction time was 23–30 h (TLC), and the products were isolated in 50–70% yield. From *p*-tolylsulfonyl azide, we obtained compounds **Vg** (R = *p*-MeC_6H_4) and **Vh** (R = *o*,*p*-$Me_2C_6H_3$). The IR spectra of the products lacked absorption in the region 1600 cm^{-1}, typical of dihydrotriazole derivatives. Therefore, they were assigned the structure of sulfonylaziridines as products of transformation of the initially formed triazoles. The formation of aziridine derivatives in reactions with azides containing electron-acceptor groups was also reported for other substituted norbornenes [6]. In the IR spectra of compounds **V** we observed absorption bands corresponding

Scheme 2.



IIa, **IIe**–**IIi** **Va**–**Vf** **Vg**, **Vh**

V, R = H (**a**), *p*-MeC_6H_4 (**b**), *o,p*-$Me_2C_6H_3$ (**c**), *m,p*-$Cl_2C_6H_3$ (**d**), *p*-$O_2NC_6H_4$ (**e**), 2-pyridyl (**f**).

to stretching vibrations of the imide carbonyl groups, as well as of the sulfonyl and nitro groups in one or both benzene rings. The aziridine ring is likely to give rise to absorption bands in the regions 1160–1190 and 860–900 cm^{-1} [6].

The ^1H NMR spectral data also confirm the presence of a fused aziridine ring in molecules **Va**, **Vd**, and **Vf**–**Vh**. Their spectra considerably differ from those of the triazole derivatives, primarily in the chemical shifts of 2-H and 4-H. In addition, the chemical shifts of the "twin" protons, 2-H/4-H and 1-H/5-H are fairly similar. The upfield shift of the *anti*-11-H signal ($\Delta\delta$ = 1.12–1.28 ppm) is also illustrative. The ^{13}C NMR spectra of **V** also showed a tendency for the chemical shifts of C^2 and C^4 to become closer (δ_C 47–50 ppm) and some similarity with the spectra of structurally related epoxy derivatives (δ_C 49–51 ppm). The signal from the bridging C^{11} atom is displaced to δ_C 31–32 ppm due to effect of the *exo*-oriented three-membered ring (aziridine or oxirane) [15].

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as KBr pellets. The ^1H NMR spectra were obtained on a Varian VXR-400 instrument operating at 400 MHz from solutions in DMSO-d_6 or chloroform-*d* using TMS as internal reference. The ^{13}C NMR spectra were measured on a Varian Gemini-BB spectrometer (100.57 MHz). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent and iodine vapor as developer. The elemental compositions were determined on a Carlo Erba analyzer.

X-Ray diffraction data for compound IIIa. Triclinic crystals, $C_{15}H_{13}N_5O_4 \cdot C_8H_5NO$, with the following unit cell parameters (20°C) a = 7.337(2), b = 11.294(3), c = 12.879(4) Å; α = 89.05(2), β = 81.09(2), γ = 87.53(2)°; V = 1053.3(5) Å^3; M 458.43; Z = 2; space group PI; d_{calc} = 1.445 g/cm^3; μ(MoK_α) = 0.106 mm^{-1}; F(000) = 476. The unit cell parameters and the intensities of 3714 reflections (3440 independent reflections with R_{int} = 0.043) were measured on a Siemens P3/PC automatic four-circle diffractometer (MoK_α irradiation, graphite monochromator, $2\theta/\theta$-scanning to $2\theta_{max} \le 50°$). The structure was solved by the direct method using SHELX97 software package [16]. The positions of hydrogen atoms were determined from the difference synthesis of electron density and were refined using the rider model with U_{iso} = 1.2U_{eq}. During the refinement, the bond lengths in the 1*H*-isoindol-1-one molecule were limited as follows: C^{1S}–C^{2S} 1.380(3), C^{2S}–C^{3S} 1.38(1), C^{3S}–C^{4S} 1.38(1), C^{4S}–C^{5S} 1.380(3), C^{5S}–C^{6S} 1.38(1), C^{1S}–C^{6S} 1.38(1), N^{1S}–C^{8S} 1.38(1), C^{8S}–O^{1S} 1.220(3), C^{6S}–C^{13S} 1.47(1), C^{13S}–N^{1S} 1.28(1) Å. The structure was refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms to wR_2 = 0.185 from 3440 reflections [R_1 = 0.062 from 1354 reflections with $F > 4\sigma(F)$, S = 0.931]. The coordinates of atoms are given in table.

N-Substituted bicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboximides IIb, IIc, IIf, and IIi (*general procedure*). Appropriate amine, 0.01 mol, was added under stirring to a solution of 0.01 mol of endic anhydride in 10 ml of benzene, and the mixture was stirred until the reaction was complete (TLC). The precipitate was filtered off, dried, and dissolved in 10 ml of glacial acetic acid, and the solution was heated under reflux until the reaction was complete (TLC). The solvent was removed under reduced pressure, water was added to the residue, and the precipitate was filtered off, dried, and recrystallized from benzene.

***N*-Isopropylbicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboximide (IIb).** Yield 71%, mp 92–93°C. Found, %: N 6.74. $C_{12}H_{15}NO_2$. Calculated, %: N 6.83.

***N-tert*-Butylbicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboximide (IIc).** Yield 66%, mp 97–98°C. IR spectrum, ν, cm^{-1}: 3030, 1710, 1680, 1565, 715. Found, %: N 6.43. $C_{13}H_{17}NO_2$. Calculated, %: N 6.39.

***N*-(*o,p*-Dimethylphenyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximide (IIf).** Yield 84%, mp 162–164°C. IR spectrum, ν, cm^{-1}: 3052, 1684, 1370, 846, 712. Found, %: N 5.05. $C_{17}H_{17}NO_2$. Calculated, %: N 5.24.

***N*-(α-Pyridyl)bicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboximide (IIi).** Yield 74%, mp 167–169°C. IR spectrum, ν, cm^{-1}: 3020, 1780, 1715, 1508, 1340. Found, %: N 11.64. $C_{14}H_{12}2\text{-}HO_2$. Calculated, %: N 11.67.

The properties of bicyclo[2.2.1]hept-5-ene-*endo*-2,-*endo*-3-dicarboximides reported previously [9] were consistent with published data.

Reaction of N-substituted bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximides IIa–IIi with *o*- and *p*-nitrophenyl azides. Equimolar amounts of the corresponding imide and azide were dissolved in chloroform, and the solution was heated under reflux until the reaction was complete (TLC). The solvent was removed, and the residue was recrystallized from 50% aqueous acetone. We thus obtained compounds **IIIa**–**IIIf** and **IVa**–**IVf**.

5-*o*-Nitrophenyl-3,4,5,10-tetraazatricyclo-[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIIa). Yield 50%, mp 128–130°C. IR spectrum, ν, cm^{-1}: 3180, 1750, 1685, 1600, 1524, 1350, 1190, 845. ^1H NMR spectrum, δ, ppm: 10.20 s (1H, NH), 7.79–7.25 (4H, H_{arom}), 4.72 d (1H, 6-H), 4.19 d (1H, 2-H), 3.40 m (1H, 8-H), 3.36 m (1H, 12-H), 3.11 m (1H, 7-H), 2.91 m (1H, 1-H), 1.68 d (1H, *syn*-13-H), 1.45 d (1H, *anti*-13-H). ^{13}C NMR spectrum, δ_C, ppm: 177.1 (C=O); 142.2, 133.4, 131.7, 125.7, 124.2, 119.0 (C_{arom}); 82.9 (C^6); 56.8 (C^2); 47.6 (C^8); 47.4 (C^{12}); 43.9 (C^7); 43.2 (C^1); 35.7 (C^{13}). Found, %: N 21.27. $C_{15}H_{13}N_5O_4$. Calculated, %: N 21.41.

10-Isopropyl-5-*o*-nitrophenyl-3,4,5,10-tetraaza-tricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIIb). Yield 72%, mp 158–159°C. ^1H NMR spectrum, δ, ppm: 7.75–7.27 (4H, H_{arom}), 4.51 d (1H, 6-H), 4.49 m (1H, *i*-Pr), 3.87 d (1H, 2-H), 3.23 m (1H, 8-H), 3.18 m (1H, 12-H), 3.14 m (1H, 7-H), 2.86 m (1H, 1-H), 1.63 d (1H, *syn*-13-H), 1.42 d (1H, *anti*-13-H), 1.38 d (6H, *i*-Pr). Found, %: N 19.12. $C_{18}H_{19}N_5O_4$. Calculated, %: N 18.97.

10-*tert*-Butyl-5-*o*-nitrophenyl-3,4,5,10-tetraaza-tricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIIc). Yield 95%, mp 188–190°C. ^1H NMR spectrum, δ, ppm: 7.75–7.23 (4H, H_{arom}), 4.56 d (1H, 6-H), 3.93 d (1H, 2-H), 3.14 m (2H, 8-H, 12-H), 3.12 m (1H, 7-H), 2.85 m (1H, 1-H), 1.60 d (1H, *syn*-13-H), 1.58 s (9H, *t*-Bu), 1.38 d (1H, *anti*-13-H). Found, %: N 18.36. $C_{19}H_{21}N_5O_4$. Calculated, %: N 18.28.

10-Benzyl-5-*o*-nitrophenyl-3,4,5,10-tetraazatri-cyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIId). Yield 54%, mp 190–191°C. IR spectrum, ν, cm^{-1}: 1760, 1700, 1690, 1605, 1530, 1360, 1170, 850. ^1H NMR spectrum, δ, ppm: 8.17–7.06 (9H, H_{arom}), 4.58 s (2H, PhC**H**$_2$), 4.28 d (1H, 6-H), 3.63 d (1H, 2-H), 3.28 m (1H, 8-H), 3.23 m (1H, 12-H), 3.12 m (1H, 7-H), 2.85 m (1H, 1-H), 1.63 d (1H, *syn*-13-H), 1.40 d (1H, *anti*-13-H). Found, %: N 16.90. $C_{22}H_{19}N_5O_4$. Calculated, %: N 16.79.

5-*o*-Nitrophenyl-10-(*p*-tolyl)-3,4,5,10-tetraazatri-cyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIIe). Yield 65%, mp 139–140°C. IR spectrum, ν, cm^{-1}: 1705, 1690, 1605, 1530, 1360, 1185, 855. ^1H NMR spectrum, δ, ppm: 7.74–7.19 (8H, H_{arom}), 4.73 d (1H, 6-H), 4.14 d (1H, 2-H), 3.47 m (1H, 8-H), 3.43 m (1H, 12-H), 3.22 m (1H, 7-H), 2.90 m (1H, 1-H), 2.42 (3H, Me), 1.72 d (1H, *syn*-13-H), 1.49 d (1H, *anti*-13-H). Found, %: N 16.65. $C_{22}H_{19}N_5O_4$. Calculated, %: N 16.79.

5-*o*-Nitrophenyl-10-(2-pyridyl)-3,4,5,10-tetraaza-tricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IIIf). Yield 71%, mp 143–144°C. IR spectrum, ν, cm^{-1}: 1715, 1705, 1600, 1590, 1530, 1360, 1185, 855. Found, %: N 20.59. $C_{20}H_{16}N_6O_4$. Calculated, %: N 20.79.

5-*p*-Nitrophenyl-3,4,5,10-tetraazatricyclo-[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVa). Yield 55%, mp 237–238°C. IR spectrum, ν, cm^{-1}: 3260, 1755, 1710, 1530, 1355, 1185, 860. ^1H NMR spectrum, δ, ppm: 11.19 s (1H, NH), 8.25 d (2H, H_{arom}), 7.32 d (2H, H_{arom}), 4.77 d (1H, 6-H), 3.94 d (1H, 2-H), 3.30 m (2H, 8-H, 12-H), 3.13 m (1H, 7-H), 3.00 m (1H, 1-H), 1.63 d (1H, *syn*-13-H), 1.20 d (1H, *anti*-13-H). Found, %: N 21.29. $C_{15}H_{13}N_5O_4$. Calculated, %: N 21.41.

10-Isopropyl-5-*p*-nitrophenyl-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVb). Yield 78%, mp 229–230°C. IR spectrum, ν, cm^{-1}: 1770, 1690, 1595, 1505, 1335, 1090, 845. ^{1}H NMR spectrum, δ, ppm: 8.25 d (2H, H_{arom}), 7.83 d (2H, H_{arom}), 4.61 d (1H, 6-H), 4.31 m (1H, *i*-Pr), 3.76 d (1H, 2-H), 3.29 m (2H, 8-H, 12-H), 3.15 m (1H, 7-H), 3.04 m (1H, 1-H), 1.65 d (1H, *syn*-13-H), 1.38 d (6H, *i*-Pr), 1.19 d (1H, *anti*-13-H). Found, %: N 19.15. $C_{18}H_{19}N_5O_4$. Calculated, %: N 18.97.

5-*p*-Nitrophenyl-10-*p*-tolyl-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVc). Yield 86%, mp 197–199°C. IR spectrum, ν, cm^{-1}: 1720, 1607, 1524, 1510, 1344, 1180, 850. ^{1}H NMR spectrum, δ, ppm: 8.17 d (2H, H_{arom}), 7.28 d (2H, H_{arom}), 7.22 d (2H, H_{arom}), 7.06 d (2H, H_{arom}), 4.83 d (1H, 6-H), 3.88 d (1H, 2-H), 3.39 m (2H, 8-H, 12-H), 3.38 m (1H, 7-H), 3.16 m (1H, 1-H), 2.32 s (3H, Me), 1.63 d (1H, *syn*-13-H), 1.36 d (1H, *anti*-13-H). ^{13}C NMR spectrum, δ_C, ppm: 175.6 (C=O); 144.4, 142.7, 139.7, 130.3, 128.6, 126.4 (C_{arom}); 83.3 (C^6); 55.9 (C^2); 46.1 (C^8); 45.9 (C^{12}); 44.2 (C^7); 43.2 (C^1); 36.1 (C^{13}); 21.6 (Me). Found, %: N 16.95. $C_{22}H_{19}N_5O_4$. Calculated, %: N 16.79.

10-(*m*,*p*-Dichlorophenyl)-5-*p*-nitrophenyl-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVd). Yield 62%, mp 185–187°C. IR spectrum, ν, cm^{-1}: 1765, 1705, 1595, 1510, 1325, 1170, 1080, 850. ^{1}H NMR spectrum, δ, ppm: 8.29 d (2H, H_{arom}), 7.70 d (2H, H_{arom}), 7.41–7.33 (3H, H_{arom}), 5.00 d (1H, 6-H), 4.23 d (1H, 2-H), 3.65 m (1H, 8-H), 3.63 m (1H, 12-H), 3.29 m (1H, 7-H), 3.23 m (1H, 1-H), 1.81 d (1H, *syn*-13-H), 1.31 d (1H, *anti*-13-H). ^{13}C NMR spectrum, δ_C, ppm: 175.2 (C=O); 145.5, 130.9, 129.5, 127.6, 126.0 (C_{arom}); 84.1 (C^6); 56.1 (C^2); 46.2 (C^8); 46.1 (C^{12}); 43.7 (C^7); 42.8 (C^1); 35.5 (C^{13}). Found, %: N 14.71. $C_{21}H_{15}Cl_2N_5O_4$. Calculated, %: N 14.83.

5,10-Bis(*p*-nitrophenyl)-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVe). Yield 57%, mp 242–244°C. Found, %: N 18.63. $C_{21}H_{16}N_6O_6$. Calculated, %: N 18.75.

5-*p*-Nitrophenyl-10-(2-pyridyl)-3,4,5,10-tetraazatricyclo[5.5.1.0$^{2,6\text{-}exo}$.0$^{8,12\text{-}endo}$]tridec-3-ene-9,11-dione (IVf). Yield 86%, mp 211–213°C. IR spectrum, ν, cm^{-1}: 1779, 1597, 1506, 1366, 1205, 1149, 843. ^{1}H NMR spectrum, δ, ppm: 7.79–7.25 (8H, H_{arom}), 4.84 d (1H, 6-H), 4.05 d (1H, 2-H), 3.56 m (2H, 8-H, 12-H), 3.20 m (1H, 7-H), 3.10 m (1H, 1-H), 1.65 d (1H, *syn*-13-H), 1.12 d (1H, *anti*-13-H). ^{13}C NMR spectrum, δ_C, ppm: 176.1 (C=O); 150.2, 126.7, 124.0, 114.1 (C_{arom}); 84.0 (C^6); 56.4 (C^2); 46.5 (C^8); 46.4 (C^{12}); 43.9 (C^7); 43.0 (C^1); 36.0 (C^{13}). Found, %: N 20.65. $C_{20}H_{16}N_6O_4$. Calculated, %: N 20.79.

Reactions of N-substituted bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboximides IIa and IIe–IIi with arylsulfonyl azides. Equimolar amounts of imide **IIa** or **IIe–IIi** and *p*-nitrophenyl- or *p*-tolylsulfonyl azide were dissolved in chloroform, and the mixture was heated under reflux until the reaction was complete (TLC). The solvent was removed, and the residue was recrystallized from isopropyl alcohol.

3-*p*-Nitrophenylsulfonyl-3,8-diazatricyclo-[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Va). Yield 84%, mp 243–245°C. IR spectrum, ν, cm^{-1}: 3260, 3045, 1755, 1710, 1530, 1355, 1327, 1185, 1170, 1095, 860. ^{1}H NMR spectrum, δ, ppm: 10.1 (1H, NH), 8.47 d (2H, H_{arom}), 8.26 d (2H, H_{arom}), 3.34 m (1H, 6-H), 3.32 m (1H, 10-H), 3.10 m (2H, 2-H, 4-H), 2.93 m (2H, 1-H, 5-H), 1.63 d (1H, *syn*-11-H), 1.25 d (1H, *anti*-11-H). ^{13}C NMR spectrum, δ_C, ppm: 176.8 (C=O); 144.0, 129.5, 124.8 (C_{arom}); 48.7 (C^2, C^4); 39.1 (C^6, C^{10}); 38.2 (C^1, C^5); 31.1 (C^{11}). Found, %: N 11.45. $C_{15}H_{13}N_3O_6S$. Calculated, %: N 11.57.

3-*p*-Nitrophenylsulfonyl-8-(*p*-tolyl)-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vb). Yield 73%, mp 158–160°C. IR spectrum, ν, cm^{-1}: 3080, 3054, 1718, 1688, 1540, 1387, 1360, 1190, 1172, 1096, 862. Found, %: N 9.20. $C_{22}H_{19}N_3O_6S$. Calculated, %: N 9.27.

8-(*o*,*p*-Dimethylphenyl)-3-*p*-nitrophenylsulfonyl-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vc). Yield 72%, mp 126–127°C. Found, %: N 8.76. $C_{23}H_{21}N_3O_6S$. Calculated, %: N 8.99.

8-(*m*,*p*-Dichlorophenyl)-3-*p*-nitrophenylsulfonyl-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vd). Yield 69%, mp 186–188°C. IR spectrum, ν, cm^{-1}: 3078, 1768, 1710, 1700, 1526, 1366, 1347, 1162, 1092, 860. ^{1}H NMR spectrum, δ, ppm: 8.43 d (2H, H_{arom}), 8.24 d (2H, H_{arom}), 7.80–7.25 (3H, H_{arom}), 3.43 m (2H, 6-H, 10-H), 3.18 m (2H, 2-H, 4-H), 3.04 m (2H, 1-H, 5-H), 1.54 d (1H, *syn*-11-H), 1.28 d (1H, *anti*-11-H). Found, %: N 8.12. $C_{21}H_{15}Cl_2N_3O_6S$. Calculated, %: N 8.27.

8-*p*-Nitrophenyl-3-*p*-nitrophenylsulfonyl-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Ve). Yield 80%, mp 177–179°C. IR spectrum, ν, cm^{-1}: 1735, 1710, 1548, 1540, 1368, 1345, 1167. Found, %: N 11.41. $C_{21}H_{16}N_4O_8S$. Calculated, %: N 11.57.

3-*p*-Nitrophenylsulfonyl-8-(2-pyridyl)-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vf). Yield 55%, mp 215–217°C. IR spectrum, ν, cm^{-1}: 3071, 1765, 1712, 1700, 1527, 1367, 1345, 1170, 1090, 860. ^{1}H NMR spectrum, δ, ppm: 8.45–7.35 (8H, H_{arom}), 3.42 m (1H, 6-H), 3.40 m (1H, 10-H), 3.07 m (2H, 2-H, 4-H), 2.97 m (2H, 1-H, 5-H), 1.61 d (1H, *syn*-11-H), 1.25 d (1H, *anti*-11-H). ^{13}C NMR spectrum, δ_C, ppm: 174.9 (C=O); 149.9, 146.9, 143.6, 138.6, 124.8, 124.5, 122.9 (C_{arom}); 47.6 (C^2, C^4); 38.9 (C^6, C^{10}); 38.8 (C^1, C^5); 31.1 (C^{11}). Found, %: N 12.64. $C_{20}H_{16}N_4O_6S$. Calculated, %: N 12.73.

8-*p*-Tolyl-3-*p*-tolylsulfonyl-3,8-diazatricyclo-[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vg). Yield 78%, mp 216–217°C. IR spectrum, ν, cm^{-1}: 3046, 1705, 1515, 1378, 1322, 1160, 1091, 881. ^{1}H NMR spectrum, δ, ppm: 7.70 d (2H, H_{arom}), 7.35 d (2H, H_{arom}), 7.15 d (2H, H_{arom}), 6.84 d (2H, H_{arom}), 3.32 m (1H, 6-H), 3.31 m (1H, 10-H), 3.23 m (2H, 2-H, 4-H), 2.76 m (2H, 1-H, 5-H), 2.34 s (3H, Me), 2.24 s (3H, Me), 1.60 d (1H, *syn*-11-H), 1.20 d (1H, *anti*-11-H). ^{13}C NMR spectrum, δ, ppm: 175.5 (C=O); 145.2, 138.6, 130.2, 129.7, 128.4, 127.0, 121.5 (C_{arom}); 49.9 (C^2, C^4); 40.1 (C^6, C^{10}); 37.7 (C^1, C^5); 31.1 (C^{11}); 20.9 (Me); 20.5 (Me). Found, %: N 6.58. $C_{23}H_{22}N_2O_4S$. Calculated, %: N 6.64.

8-(*o,p*-Dimethylphenyl)-3-*p*-tolylsulfonyl-3,8-diazatricyclo[5.3.1.0$^{2,4\text{-}exo}$.0$^{6,10\text{-}endo}$]undecane-7,9-dione (Vh). Yield 51%, mp 176–178°C. IR spectrum, ν, cm^{-1}: 1708, 1507, 1380, 1324, 1163, 1069, 880. ^{1}H NMR spectrum, δ, ppm: 7.71 d (2H, H_{arom}), 7.28 d (2H, H_{arom}), 7.07–6.80 (3H, H_{arom}), 3.25 m (2H, 6-H, 10-H), 3.10 m (2H, 2-H, 4-H), 3.02 m (2H, 1-H, 5-H), 2.39 s (3H, Me), 2.28 s (3H, Me), 2.00 s (3H, Me), 1.79 d (1H, *syn*-11-H), 1.12 d (1H, *anti*-11-H). Found, %: N 6.33. $C_{24}H_{24}N_2O_4S$. Calculated, %: N 6.42.

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