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Synthesis of Amines from Norbornane Series

E.A. Yatsynich[1], D.V. Petrov[1], V.A. Dokichev[1], and Yu.V. Tomilov[2]

[1]*Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences*
Ufa, 450054 Russia;
e-mail: dokichev@anrb.ru
[2]*Zelinsky Institute of Organic Chemistry, Russian Academy of Science*

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Abstract—Synthetic procedure was developed for preparation of *exo*-oriented di- and tetraamines of the norbornane series by 1,3-dipolar cycloaddition to norbornene and norbornadiene of generated *in situ* diazomethane followed by reduction of arising pyrazolines catalyzed by Raney nickel.

A propylenediamine fragment is among the structures frequently occurring in pharmaceuticals used in treating the central nervous system [for instance, antidepressant Impramin (Tofranil)] [1]. The propylenediamine is exclusively active in prototropic reactions [2]. This reagent initiates the exceptionally fast migration of a triple bond from the middle of a carbon chain to the terminal position (the so-called "acetylene zipper") [2]. The syntheses of new compounds of this series are extensively devised as a rule by reactions of alkyl halides with 1,3-diaminopropanes [3], catalytic hydrogenation of pyrazolines [4], and reduction of hexahydripyrimidines [5]. Di- and tetraamines of norbornane series are promising as monomers for preparation of polyamides with a three-dimensional structure [6] and of polyaminocarboxylic acids that are widely used in separation and analysis of transition metal cations [7, 8]. This kind of norbornane derivatives and the products of their chemical modification are also valuable as potential biologically active compounds [9].

In this study in extension of our investigations in the field of the chemistry of aliphatic diazo compounds [10–12] and with a goal to develop a synthesis of norbornanes containing in their structure an *exo*-directed propylenediamine fragment we carried out reactions of bicyclo-[2.2.1]hept-2-ene and bicyclo-[2.2.1]hepta-2,5-diene with diazomethane generated *in situ* from *N*-methyl-*N*-nitrosourea with subsequent hydrogenation of pyrasolines obtained. It is significant that at the time we have begun our studies no data has been published on the synthesis of di- and tetraamines of the norbornane series containing *exo*-oriented amino or aminomethyl groups in the positions *2, 3* and *5, 6* of the norbornane skeleton.

We formerly [13] developed a procedure for direct catalytic cyclopropanation of strained cycloalkenes with diazomethane generated *in situ* in strong alkaline medium when the diazomethane formation and decomposition effected by catalytic metal complexes in the organic phase occur in parallel. In extension of the concept of simplifying chemical processes by combining the stages of diazomethane generation and its simultaneous conversion in practically useful compounds we applied this procedure to the synthesis of pyrazolines of norbornane series. As a result of a stereoselective 1,3-dipolar cycloaddition of diazomethane to norbornene at –5°C in Et_2O solution *exo*-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**I**) was obtained in a 98% yield. No 2-pyrazolines were detected in the reaction mixture that could have formed by isomerization of 1-pyrazolines under the action of KOH.

The structure of compound **I** was proved by ^{1}H and ^{13}C NMR spectroscopy using the procedures ^{1}H–^{1}H COSY and CHCORR. The *exo*-position of the pyrazoline fragment of the molecule is evidenced by the zero values of coupling constants $^3J_{1,2}$ and $^3J_{6,7}$ and by the chemical shift of the C^{10} atom of the methylene group (30.97 ppm) [14]. A long-distance coupling is observed between the *endo*-directed proton H^2 and *cis*-H^5 and *transC*-H^5 protons with the coupling constants 1.2 and 3.4 Hz respectively.

The study of the N=N bond reduction in compound **I** demonstrated that the zinc powder in acetic acid [15] did not reduce the N=N bond, and $NaBH_4$ in CH_3OH

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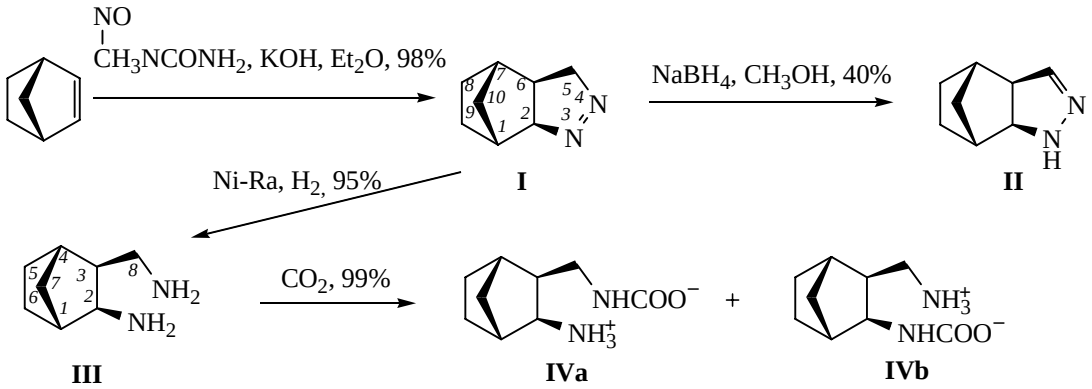
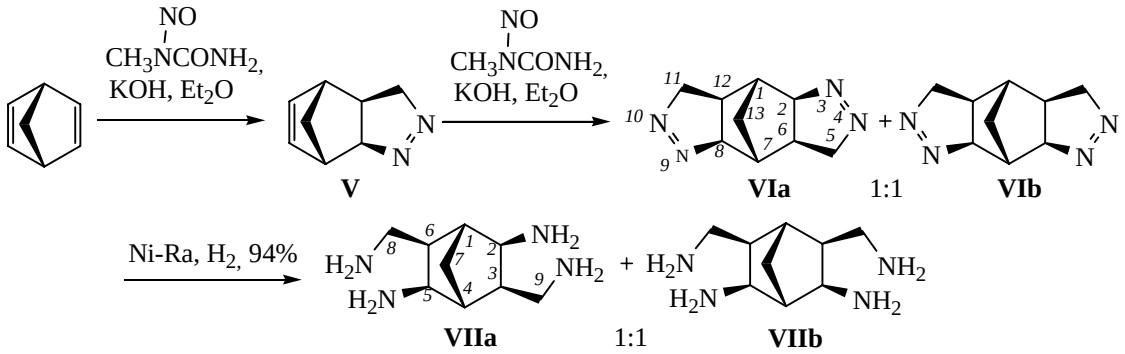
Scheme 1.



Scheme 2.



[16] effected isomerization of pyrazoline **I** into pyrazoline **II**. The hydrogenation of *exo*-3,4-diazatricyclo-[5.2.1.$0^{2,6}$]dec-3-ene (**I**) into *exo*-2-amino-*exo*-3-aminomethylicyclo[2.2.1]heptane (**III**) with hydrogen succeeded only at the use of heterogenous catalysts. Pyrazoline **I** was converted into diamine **III** in a 95% yield by hydrogenation on the Raney nickel at 100°C and hydrogen pressure 115 at. The application of PtO_2 resulted in a 54% yield of diamine **III**. The data of elemental analysis and the IR spectrum (the lack of characteristic band of the N=N bond in the region 1550–1560 cm^{-1}, and the presence of bands at 3400–3080 and 1584 cm^{-1} belonging to NH_2 groups) confirm that the reduction occurs with the cleavage of the N=N bond.

In the course of study we observed the ability of diamine **III** to absorb CO_2 from air at room temperature transforming into a mixture of isomeric carbamates **IVa** and **IVb** in a ratio 1:1 apparently through the intermediate formation of carbonates [17].

The reaction of diazomethane generated *in situ* from N-methyl-N-nitrosourea with norbornadiene afforded isomeric bis-pyrazolines in an overall yield 44%. At the use of triple molar excess of norbornadiene we isolated from the reaction mixture diadducts **VIa** and **VIb** and monoadduct **V** in an overall yield 55% at the ratio 1:1:3 respectively. Compound **V** unlike the norbornadiene monoadduct with methyl diazoacetate [18] did not transform into pyrazole at room temperature.

Pyrazoline fragment in monoadduct **V** did not affect the regioselectivity of the cycloaddition of the second CH_2N_2 molecule to the norbornene bond as showed the formation of diadducts **VIa** and **VIb** in equimolar quantities notwithstanding the molar ratio norbornadiene–N-methyl-N-nitrosourea. The reaction of norbornadiene with a double excess of diazomethane gave rise to the isomeric mixture of pirazolines **VIa** and **VIb** in a 85% yield, and on standing for 72 h a crystalline mixture of adducts precipitated enriched with isomer **VIa** (6.7:1). The zero values of coupling constants $^3J_{1,2}$ and $^3J_{6,7}$ in compounds **V**, $^3J_{1,2}$, $^3J_{6,7}$, $^3J_{8,9}$, and $^3J_{1,12}$ in compound **VIa**, and $^3J_{1,2}$, $^3J_{6,7}$, $^3J_{8,9}$, $^3J_{1,12}$ in compound **VIb** confirm the *exo*-configuration of the structure.

The hydrogenation of tetraazaheterocycles **VIa** and **VIb** on Raney nickel at 100°C furnished a difficult-to separate mixture of tetraamines **VIIa** and **VIIb** in an overall yield 94%.

Hence by reaction of norbornene (norbornadiene) and diazomethane generated *in situ* from *N*-methyl-*N*-nitrosourea followed by hydrogenation of the pyrazolines obtained we prepared for the first time di- and tetraamines of the norbornane series containing *exo*-oriented amino and aminomethyl groups in the positions *2*, *3* and *5*, *6* of the norbornane skeleton.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 (at 300.13 and 75.47 MHz respectively), internal reference TMS. IR spectra were recorded on spectrophotometer Specord M-80 from thin films or mulls in mineral oil. Melting point were measured on Bo¸tius heating block. GLC was carried out on a chromatograph Chrom-5 with a flame-ionization detector [column 1200×5 mm, 5% SE-30 on solid carrier Inerton N-AW DMCS (0.125–0.160 mm)], carrier gas helium.

Norbornene was prepared by the known procedure [19]. Commercial norbornadiene was used (product of OAO "Salavatnefteorgsintez").

***exo*-3,4-Diazatricyclo[5.2.1.0^{2,6}]dec-3-ene (I)**. To a mixture of 75 ml of 40% water solution of KOH, 250 ml of ethyl ether, and 10 g (0.106 mol) of norbornene at –5°C while constant stirring was added within 1 h by small portions 25 g (0.243 mol) of *N*-methyl-*N*-nitrosourea. In 24 h the ether layer was separated and dried over KOH for 30 min. On removing the ether the residue was distilled in a vacuum. We obtained 13.9 g (98%) of pyrazoline **I**, bp 96°C (10 mm Hg), n_D^{20} 1.5098. IR spectrum, ν, cm^{-1}: 1548 (N=N), 2872–2960. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.46 d.d.d (1H, H^{10a}, $^2J_{10a,10s}$ 10.7, $^4J_{10a,2}$ 1.4, $^4J_{10a,6}$ 1.6 Hz), 0.89 d.d.d (1H, H^{10s}, $^2J_{10s,10a}$ 10.7, $^4J_{10s,8n}$ 1.8, $^4J_{10s,9n}$ 1.6 Hz), 1.16 d.d.d.d (1H, H^{8n}, $^2J_{8n,8x}$ 11.8, $^3J_{9n,8n}$ 8.4, $^3J_{8n,9x}$ 4.4, $^4J_{8n,10s}$ 1.8 Hz), 1.30 d.d.d.d (1H, H^{9n}, $^2J_{9n,9x}$ 10.9, $^3J_{8n,9n}$ 8.4, $^3J_{9n,8x}$ 4.1, $^4J_{9n,10s}$ 1.6 Hz), 1.39 t.t (1H, H^{8s}, $^2J_{8n,8x}$ = $^3J_{9x,8x}$ 11.8, $^3J_{8x,9n}$ = $^3J_{8x,7}$ 4.1 Hz), 1.55 d.d.d.d (1H, H^{9x}, $^2J_{9n,9x}$ 10.9, $^3J_{9n,8x}$ 11.8, $^3J_{8n,9x}$ 4.4, $^3J_{9x,1}$ 4.1 Hz), 1.74 d.d.d.d (1H, H^6, $^3J_{6,5cis}$ 9.7, $^3J_{6,2}$ 7.2, $^3J_{6,5trans}$ 3.4, $^4J_{10a,6}$ 1.6 Hz), 1.90 br.s (1H, H^7), 2.72 br.d (1H, H^1, $^3J_{9x,1}$ 4.1 Hz), 3.94 d.d.d (1H, H^{5trans}, $^2J_{5cis,5trans}$ 18.4, $^3J_{5trans,6}$ 3.4, $^4J_{5trans,2}$ 3.4 Hz), 4.43 d.d.d (1H, H^{5cis}, $^2J_{5cis,5trans}$ 18.4, $^3J_{5cis,6}$ 9.7, $^4J_{5cis,2}$ 1.2 Hz), 4.50 d.d.d.d (1H, H^2, $^3J_{6,2}$ 7.2, $^4J_{5trans,2}$ 3.4, $^4J_{10a,2}$ 1.4, $^4J_{5cis,2}$ 1.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.86 (C^9), 27.74 (C^8), 30.97 (C^{10}), 37.50 (C^6), 38.77 (C^1), 40.87 (C^7), 82.47 (C^5), 96.45 (C^2). Found, %: C 70.46; H 8.80; N 20.61. $C_8H_{12}N_2$. Calculated, %: C 70.56; H 8.88; N 20.56.

***exo*-3,4-Diazatricyclo[5.2.1.0^{2,6}]dec-4-ene (II).** To a solution of 1 g (0.007 mol) of pyrazoline **I** in 30 ml of MeOH cooled to 0°C was added at stirring within 15 min by small portions 1.125 g (0.03 mol) of $NaBH_4$. In 1 h the solvent was distilled off, 5 ml of water was added to the reaction mixture, and it was boiled for 1 h. The reaction mixture was filtered, and by continuous extraction with Et_2O 0.4 g (40%) of pyrazoline **II** was separated, yellow crystals, mp 63°C. IR spectrum, ν, cm^{-1}: 1592 (C=N), 2872–2960, 3280 (N–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 m (1H, H^{9n}), 1.11 m (1H, H^{8n}), 1.17 d (1H, H^{10a}, $^2J_{10a,10s}$ 8.3 Hz), 1.30 d.d.d (1H, H^{10s}, $^2J_{10s,10a}$ 8.3, $^4J_{10s,8n}$ 1.6, $^4J_{10s,9n}$ 1.9 Hz), 1.40 m (1H, H^{9x}), 1.51 m (1H, H^{8x}), 2.24 br.s (1H, H^7), 2.29 br.s (1H, H^1), 3.00 d (1H, H^6, $^3J_{6,2}$ 9.2 Hz), 3.58 d (1H, H^2, $^3J_{6,2}$ 9.2 Hz), 4.29 br.s (1H, NH), 6.57 s (1H, H^5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.90 (C^9), 28.04 (C^8), 32.58 (C^{10}), 39.54 (C^7), 43.78 (C^1), 57.13 (C^6), 63.43 (C^2), 146.26 (C^5). Found, %: C 71.05; H 8.31; N 20.60. $C_8H_{16}N_2$. Calculated, %: C 70.55; H 8.88; N 20.57.

***exo*-2-Amino-*exo*-3-aminomethylbicyclo-[2.2.1]-heptane (III).** Into a steel pressure reactor (*V* 100 cm^3) was charged 2 g (0.015 mol) of pyrazoline **I**, 50 ml of MeOH, and 0.06 g of Ni-Ra. The hydrogenation was carried out at H_2 pressure 115 at and temperature 100°C for 6 h. The reaction mixture was filtered, the solvent was evaporated, the residue was distilled in a vacuum. We obtained 1.95 g (95%) of diamine **III**, bp 68°C (2 mm Hg), n_D^{20} 1.6243. IR spectrum, cm^{-1}: 1584 (NH bend.), 2872–2952, 3400–3080 (NHstretch.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 d.d.d (1H, H^{7a}, $^2J_{7a,7s}$ 10.2, $^3J_{7a,4}$ 1.2, $^4J_{7a,2}$ 1.2 Hz), 1.04 d (1H, H^{6n}, $^2J_{6n,6x}$ 8.6 Hz), 1.05 d (1H, H^{5n}, $^2J_{5n,5x}$ 8.6 Hz), 1.24 br.s (4H, NH_2), 1.38 d.d (1H, H^{5x}, $^2J_{5n,5x}$ 8.6, $^3J_{5x,4}$ 3.3 Hz), 1.41 d.d (1H, H^{6x}, $^2J_{6n,6x}$ 8.6, $^3J_{6x,1}$ 3.5 Hz), 1.47 d.d.d (1H, H^3, $^3J_{3,2}$ 7.8, $^3J_{3,8cis}$ 9.1, $^3J_{3,8trans}$ 6.4 Hz), 1.48 d.d (1H, H^{7s}, $^2J_{7a,7s}$ 10.2, $^3J_{7s,1}$ 1.2 Hz), 1.86 m (2H, H^1, H^4), 2.54 d.d (1H, H^{8trans}, $^2J_{8cis,8trans}$ 12.2, $^3J_{8trans,3}$ 6.4 Hz), 2.65 d.d (1H, H^{8cis}, $^2J_{8trans,8cis}$ 12.2, $^3J_{8cis,3}$ 9.1 Hz), 2.91 d.d (1H, H^2, $^3J_{3,2}$ 7.8, $^4J_{7a,2}$ 1.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.89 (C^6), 29.18 (C^5), 32.01 (C^7), 39.46 (C^4), 41.74 (C^8), 45.79 (C^1), 50.24 (C^3), 56.82 (C^2). Found, %: C 67.5; H 10.6; N 19.7. $C_8H_{16}N_2$. Calculated, %: C 68.52; H 11.50; N 19.98.

***exo*-{(*exo*-3-Ammoniobicyclo[2.2.1]hept-2-yl)-methyl} carbamate (IVa) and *exo*-{*exo*-(3-ammonio-methyl)bicyclo[2.2.1]hept-2-yl} carbamate (IVb).** From 0.5 g (0.004 mol) of diamine **III** at storage in air at 20°C in 96 h formed 0.65 g (99%) of colorless crystals

of compounds **IVa** and **IVb** in a ratio 1:1, mp 138–142°C. IR spectrum, ν, cm^{-1}: 1456 (CO_2^- bend.), 1504 (NH_3^+ bend.), 1576 (NH bend.), 1642 (CO_2^- stretch.), 2182 (NH_3^+ stretch.), 2854–2944, 3298–3334 (NH_2). Found, %: C 57.93; H 8.62; N 15.52. $C_9H_{16}N_2O_2$. Calculated, %: C 58.67; H 8.75; N 15.21.

***exo*-{(*exo*-3-Ammoniobicyclo[2.2.1]hept-2-yl)methyl} carbamate (IVa).** ^{1}H NMR spectrum (D_2O), δ, ppm: 1.14 d (1H, H^{7a}, $^2J_{7a,7s}$ 9.8 Hz), 1.18 m (2H, H^{5n}, H^{6n}), 1.44 d (1H, H^{7s}, $^2J_{7s,7a}$ 9.8 Hz), 1.81 d.d.d (1H, H^{2n}, $^3J_{2n,8trans}$ 5.8, $^3J_{2n,8cis}$ 7.2, $^3J_{2n,3n}$ 7.3 Hz), 1.52 m (2H, H^{5x}, H^{6x}), 2.09 br.s (2H, H^1, H^4), 2.74 d.d (1H, H^{8trans}, $^3J_{8trans,2n}$ 5.8, $^2J_{8trans,8cis}$ 12.8 Hz), 2.85 d.d (1H, H^{8cis}, $^3J_{8cis,3n}$ 7.2, $^2J_{8cis,8trans}$ 12.8 Hz), 3.55 d (1H, H^{3n}, $^3J_{2n,3n}$ 7.3 Hz). ^{13}C NMR spectrum (D_2O), δ, ppm: 28.59 (C^5), 31.04 (C^6), 35.50 (C^7), 41.76 (C^1), 42.46 (C^8), 45.39 (C^4), 49.16 (C^2), 59.59 (C^3), 167.06 (CO_2^-).

***exo*-{*exo*-(3-Ammoniomethyl)bicyclo[2.2.1]hept-2-yl)methyl} carbamate (IVb).** ^{1}H NMR spectrum (D_2O), δ, ppm: 1.14 d (1H, H^{7a}, $^2J_{7a,7s}$ 9.8 Hz), 1.18 m (2H, H^{5n}, H^{6n}), 1.44 d (1H, H^{7s}, $^2J_{7s,7a}$ 9.8 Hz), 1.88 d.d.d (1H, H^{3n}, $^3J_{3n,8trans}$ 5.8, $^3J_{3n,8cis}$ 7.2, $^3J_{3n,2cis}$ 7.3 Hz), 1.52 m (2H, H^{5x}, H^{6x}), 2.05 br.s (1H, H^1), 2.09 br.s (1H, H^4), 2.74 d.d (1H, H^{8trans}, $^3J_{8trans,3n}$ 5.8, $^2J_{8trans,8cis}$ 12.8 Hz), 2.85 d.d (1H, H^{8cis}, $^3J_{8cis,3n}$ 7.2, $^2J_{8cis,8trans}$ 12.8 Hz), 3.03 d (1H, H^{2n}, $^3J_{2n,3n}$ 7.8 Hz). ^{13}C NMR spectrum (D_2O), δ, ppm: 28.41 (C^6), 30.86 (C^5), 34.26 (C^7), 41.39 (C^4), 42.16 (C^8), 46.61 (C^1), 48.11 (C^3), 58.82 (C^2), 167.00().

Reaction of norbornadiene with CH_2N_2. (a) Generation of CH_2N_2 *in situ* from *N*-methyl-*N*-nitrosourea. To a mixture of 40.2 ml of 40% water solution of KOH, 134 ml of ethyl ether, and 2 g (0.022 mol) of norbornadiene at –5°C while continuous stirring was added by small portions 13.42 g (0.130 mol) of *N*-methyl-*N*-nitrosourea. In 24 h the ether layer was separated and dried over KOH for 30 min, filtered, and left standing for 48 h. The precipitated colorless crystals were filtered off, washed with 10 ml of ether to obtain 1.68 g (44%) of a mixture of pyrazolines **VIa** and **VIb** in a ratio 1:1, mp 78–80°C. IR spectrum, ν, cm^{-1}: 1546 (N=N), 2852–2926. Found, %: C 61.46; H 6.75; N 31.78. $C_8H_{12}N_2$. Calculated, %: C 61.34; H 6.87; N 31.79.

***b*. At a molar ratio 3:1.** To a solution of 3 g (0.033 mol) of norbornadiene in 10 ml of Et_2O was added 23 ml (0.457 g, 0.011 mol) of ether solution of CH_2N_2, and the mixture was stirred for 24 h. The solvent was evaporated to get 0.66 g of a mixture of pyrazolines **V, VIa,** and **VIb** in yields 34, 10.5, and 10.5% respectively.

***exo*-3,4-Diazatricyclo[5.2.1.0^{2,6}]deca-3,8-diene (V).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.63 d (1H, H^{10a}, $^2J_{10a,10s}$ 9.4 Hz), 1.31 d (1H, H^{10s}, $^2J_{10a,10s}$ 9.4 Hz), 2.03 d.d.d (1H, H^6, $^3J_{6,5cis}$ 9.7, $^3J_{6,2}$ 7.3, $^3J_{6,5trans}$ 3.4 Hz), 2.49 c (1H, H^7), 3.32 c (1H, H^1), 3.92 d.d.d (1H, H^{5trans}, $^2J_{5cis,5trans}$ 18.4, $^3J_{5trans,6}$ 3.4, $^4J_{5trans,2}$ 3.4 Hz), 4.21 d.d.d (1H, H^{5cis}, $^2J_{5cis,5trans}$ 18.4, $^3J_{5cis,6}$ 9.7, $^4J_{5cis,2}$ 1.2 Hz), 4.61 d.d.d (1H, H^2, $^3J_{6,2}$ 7.2, $^4J_{5cis,2}$ 1.2, $^4J_{5trans,2}$ 3.4 Hz), 6.07 d (1H, H^8, $^3J_{8,9}$ 6.7 Hz), 6.08 d (1H, H^9, $^3J_{8,9}$ 6.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 37.66 (C^1), 41.21 (C^{10}), 44.66 (C^7), 45.75 (C^6), 77.38 (C^5), 98.14 (C^2), 134.97 (C^8), 140.02 (C^9).

***exo,exo*-3,4,9,10-Tetraazatetracyclo-[5.5.1.0^{2,6}0^{8,12}]trideca-3,9-diene (VIa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.26 s (1H, H^{13}), 2.04 d.d.d (2H, H^6, H^{12}, $^3J_{6,2} = {}^3J_{12,8}$ 7.3, $^3J_{6,5cis}$ 9.7, $^3J_{12,11cis}$ 9.7, $^3J_{6,5trans}$ 3.4, $^3J_{12,11trans}$ 3.4 Hz), 2.5 c (2H, H^1, H^7), 4.04 d.d.d (2H, H^{5trans}, $H^{11trans}$, $^2J_{5cis,5trans}$ 18.6, $^2J_{11cis,11trans}$ 18.6, $^3J_{5trans,6}$ 3.4, $^3J_{11trans,12}$ 3.4, $^4J_{5trans,2}$ 3.4, $^4J_{11trans,8}$ 3.4 Hz), 4.49 d.d.d (2H, H^{5cis}, H^{11cis}, $^2J_{5cis,5trans} = {}^2J_{11cis,11trans}$ 18.6, $^3J_{5cis,6} = {}^3J_{11cis,12}$ 9.7, $^4J_{5cis,2} = {}^4J_{11cis,8}$ 1.3 Hz), 4.61 d.d.d (2H, H^2, H^8, $^4J_{5trans,2} = {}^4J_{11trans,8}$ 3.4, $^3J_{2,6} = {}^3J_{8,12}$ 7.3, $^4J_{5cis,2} = {}^4J_{11cis,8}$ 1.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.47 (C^{13}), 35.21 (C^1, C^7), 37.31 (C^6, C^{12}), 81.36 (C^5, C^{11}), 94.04 (C^2, C^8).

***exo,exo*-3,4,10,11-Tetraazatetracyclo-[5.5.1.0^{2,6}0^{8,12}]trideca-3,10-diene (VIb).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.26 C (1H, H^{13}), 1.72 C (1H, H^7), 1.86 d.d.d (2H, H^6, H^8, $^3J_{6,2} = {}^3J_{12,8}$ 7.3, $^3J_{6,5cis} = {}^3J_{8,9cis}$ 9.7, $^3J_{6,5trans} = {}^3J_{8,9trans}$ 3.4 Hz), 3.33 c (1H, H^1), 3.92 d.d.d (2H, H^{5trans}, H^{9trans}, $^2J_{5trans,5cis} = {}^2J_{9trans,9cis}$ 18.4, $^3J_{5trans,6} = {}^3J_{9trans,8}$ 3.4, $^4J_{5trans,2} = {}^4J_{9trans,\ 12}$ 3.4 Hz), 4.42 d.d.d (2H, H^{5cis}, H^{9cis}, $^2J_{5cis,5trans} = {}^2J_{9cis,9trans}$ 18.4, $^3J_{5cis,6} = {}^3J_{9cis,8}$ 9.7, $^4J_{5cis,2} = {}^4J_{9cis,12}$ 1.4 Hz), 4.82 d.d.d (2H, H^2, H^{12}, $^4J_{5trans,2} = {}^4J_{9trans,12}$ 3.4, $^3J_{2,6} = {}^3J_{8,12}$ 7.3, $^4J_{5cis,2} = {}^4J_{12cis,9}$ 1.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.47 (C^{13}), 41.74 (C^7), 43.29 (C^6, C^8), 45.23 (C^1), 81.51 (C^5, C^9), 95.67 (C^2, C^{12}).

Reduction of *exo,exo*-3,4,10,11-tetraazatetracyclo[5.5.1.0^{2,6}0^{8,12}]trideca-3,10-diene (VIa) and *exo,exo*-3,4,9,10-tetraazatetracyclo-[5.5.1.0^{2,6}0^{8,12}]-trideca-3,9-diene (VIb). Into a steel pressure reactor (*V* 100 cm^3) was charged 1.68 g (9.5 mmol) of a mixture of compounds **VIa** and **VIb**, 50 ml of MeOH, and 0.12 g of Ni-Ra. The hydrogenation was carried out at H_2 pressure 115 at and temperature 100°C for 6 h. The reaction mixture was filtered, the solvent was evaporated to obtain 1.65 g (94%) of oily mixture of tetraamines **VIIa** and **VIIb** that within 24 h crystallized, mp 30–32°C.

IR spectrum, ν, cm^{-1}: 2854–2920, 3328–3400 (NH stretch.). Found, %: C 58.63; H 10.97; N 30.37. $C_8H_{12}N_2$. Calculated, %: C 58.66; H 10.94; N 30.40.

***exo,exo*-2,5-Diamino-*exo,exo*-3,6-diaminomethylbicyclo[2.2.1]heptane (VIIa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 s (2H), 1.66 d.d.d (2H, H^3, H^6, $^3J_{3,2} = {}^3J_{5,6}$ 7.8, $^3J_{3,9cis} = {}^3J_{6,8cis}$ 7.6, $^3J_{3,9trans} = {}^3J_{6,8trans}$ 7.6 Hz), 1.83 m (2H, H^1, H^4), 2.59 d.d (2H, H^{8trans}, H^{9trans}, $^2J_{8cis,8trans} = {}^2J_{9cis,9trans}$ 12.6, $^3J_{9trans,3} = {}^3J_{8trans,6}$ 7.6 Hz), 2.75 d.d (2H, H^{8cis}, H^{9cis}, $^2J_{8cis,8trans} = {}^2J_{9cis,9trans}$ 12.6, $^3J_{9cis,3} = {}^3J_{8cis,6}$ 7.6 Hz), 2.95 d (2H, H^2, H^5, $^3J_{3,2} = {}^3J_{5,6}$ 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.48 (C^7), 41.92 (C^8, C^9), 48.95 (C^1, C^4), 51.88 (C^3, C^6), 55.93 (C^2, C^5).

***exo,exo*-2,6-Diamino-*exo,exo*-3,5-diaminomethylbicyclo[2.2.1]heptane (VIIb).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 s (2H, H^7), 1.66 d.d.d (2H, H^3, H^5, $^3J_{3,2} = {}^3J_{5,6}$ 8.1, $^3J_{3,9cis} = {}^3J_{5,8cis}$ 7.6, $^3J_{3,9trans} = {}^3J_{5,8trans}$ 7.6 Hz), 1.81 br.s (1H, H^4), 1.94 br.s (1H, H^1), 2.59 d.d (2H, H^{8trans}, H^{9trans}, $^2J_{8cis,8trans} = {}^2J_{9cis,9trans}$ 12.6, $^3J_{9trans,3} = {}^3J_{8trans,5}$ 7.6 Hz), 2.75 d.d (2H, H^{8cis}, H^{9cis}, $^2J_{8cis,8trans} = {}^2J_{9cis,9trans}$ 12.6, $^3J_{9cis,3} = {}^3J_{8cis,5}$ 7.6 Hz), 2.99 d (2H, H^2, H^6, $^3J_{3,2} = {}^3J_{5,6}$ 8.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.48 (C^7), 41.92 (C^8, C^9), 44.03 (C^4), 50.20 (C^1), 51.88 (C^3, C^5), 57.99 (C^2, C^6).

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