

Synthesis of 1-Benzyl-3,6-diazahomoadamantane

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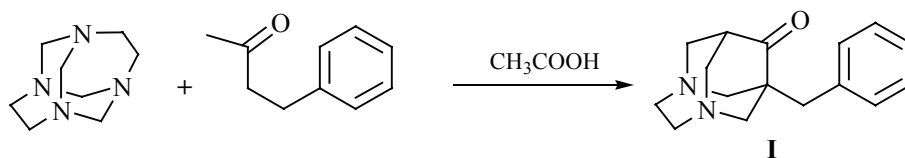
Abstract—Condensation of 4-phenylbutan-2-one with tetramethylenediethylenetetramine afforded 1-benzyl-3,6-diazahomoadamantan-9-one, whose nitration provided 1-(4-nitrobenzyl)-3,6-diazahomoadamantan-9-one. The modification of the nitro and carbonyl groups resulted in the formation of 1-benzyl-3,6-diazahomoadamantane and its derivatives with functional groups at the benzene ring and the bridging carbon atom C⁹.

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We reported on the synthesis of some derivatives of 3,6-diazahomoadamantan-9-one with substituents at the nodal atom C¹ by the condensation of methyl ketones with tetramethylenediethylenetetramine and on their further transformations into 3,6-diazahomoadamantane [1] and its derivatives [2].

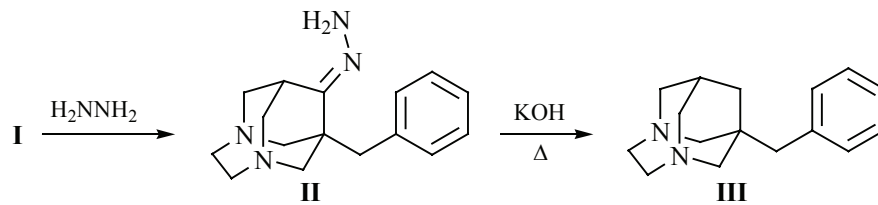
In extension of the research on the synthesis of new derivatives of 3,6-diazahomoadamantane we obtained by the condensation of 4-phenylbutan-2-one with tetramethylenediethylenetetramine 1-benzyl-3,6-diazahomoadamantan-9-one (**I**). Its ¹H NMR spectrum contains the group of signals characteristic of the diazahomoadamantane scaffold consisting of two AB

systems of protons NCH₂C, the multiplet of the protons of the ethylene bridge NCH₂CH₂N, and the broadened singlet at 2.65 ppm from the proton located in the nodal position. The benzyl group signal appears as a singlet of the methylene group protons at 2.85 ppm and a multiplet of the benzene group protons in the region 7.10–7.35 ppm. In the IR spectrum the absorption bands are observed of the stretching vibrations of the carbonyl groups in the region 1707 cm⁻¹ and of benzene ring in the region 1605 cm⁻¹. The mass spectrum contains the molecular ion peak ([M]⁺ 256), whose main fragmentation occurs as the skeleton decomposition and the formation of cations with *m/z* 72 and 58.



The hydrazone of ketone **II** was subjected to Kishner–Wolff reduction into 1-benzyl-3,6-diazahomoadamantane (**III**) [3]. In the mass spectrum of benzyldiazahomoadamantane (**III**) the molecular ion peak was present ([M]⁺ 242), whose main fragmentation was governed by the rupture of the bond between the benzyl substituent and the scaffold and by the formation of cations with *m/z* 151 and

91. In the ¹H NMR spectrum the proton in the nodal position of the scaffold gave rise to a singlet at 1.85 ppm, two protons of the methylene from the benzyl group appeared as a singlet at 2.35 ppm, the protons of the ethylene fragment NCH₂CH₂N, as a multiplet at 3.05 ppm. Four doublets at 2.60, 2.95, 3.15, and 2.70 ppm correspond to the protons of four methylene groups NCH₂C. The

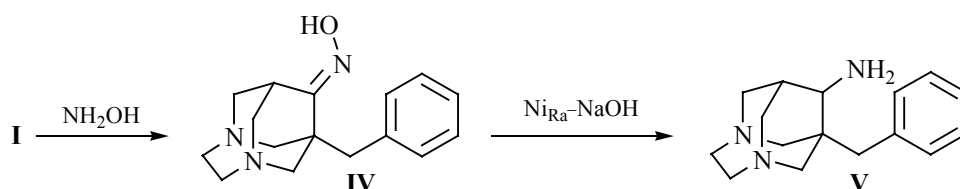


protons of the methylene group of the scaffold CCH_2C are observed as a singlet at 1.60 ppm.

The treatment of ketone **I** with hydroxylamine afforded 1-benzyl-3,6-diazahomoadamantan-9-one oxime (**IV**) whose IR spectrum contained the absorption

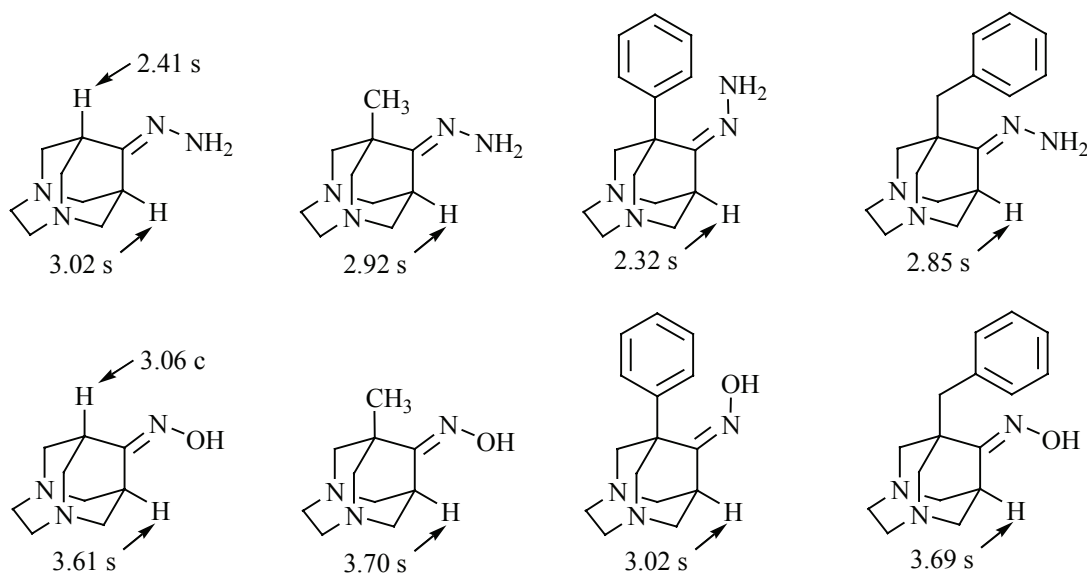
bands of stretching vibrations of azomethine and hydroxy groups at 1630 and 3220 cm^{-1} respectively.

Oxime **IV** was reduced with nickel–aluminum alloy [4] (50 : 50) (Raney alloy) in water-alkaline medium into 1-benzyl-3,6-diazahomoadamantan-9-amine (**V**).



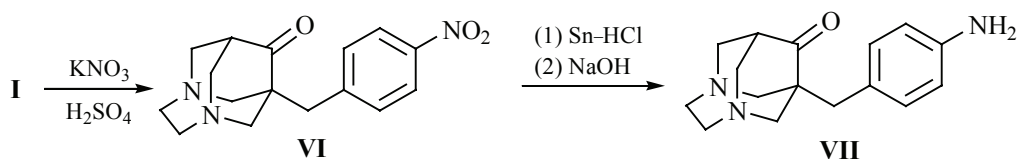
The comparison of the values of the chemical shifts of protons attached to the atom C^8 in the spectra of hydrazone **II** and oxime **IV** and the other analogous derivatives of diazahomoadamantane [3, 5] allows a

conclusion that the double bond in compounds **II**, **IV** with a benzyl group possesses the *E*-configuration. When a phenyl is present instead of the benzyl group, the π -bond has the *Z*- configuration [5].



The nitration of benzyl-diazahomoadamantanone (**I**) with a mixture of potassium nitrate and sulfuric acid [6] led to the formation of 1-(4-nitrobenzyl)-3,6-

diazahomoadamantan-9-one (**VI**) that was reduced with tin in hydrochloric acid into 1-(4-aminobenzyl)-3,6-diazahomoadamantan-9-one (**VII**).



The IR spectrum of nitroketone **VI** contains absorption bands of the stretching vibrations of the nitro group in the region 1514, 1350 cm^{-1} and the carbonyl group at 1697 cm^{-1} . Mass spectra of compounds **VI** and **VII** contain the molecular ion peaks ($[M]^+$ 301) and ($[M]^+$ 271), whose main fragmentation occurs as the skeleton decomposition and the formation of cations with m/z 42, 58, and 72.

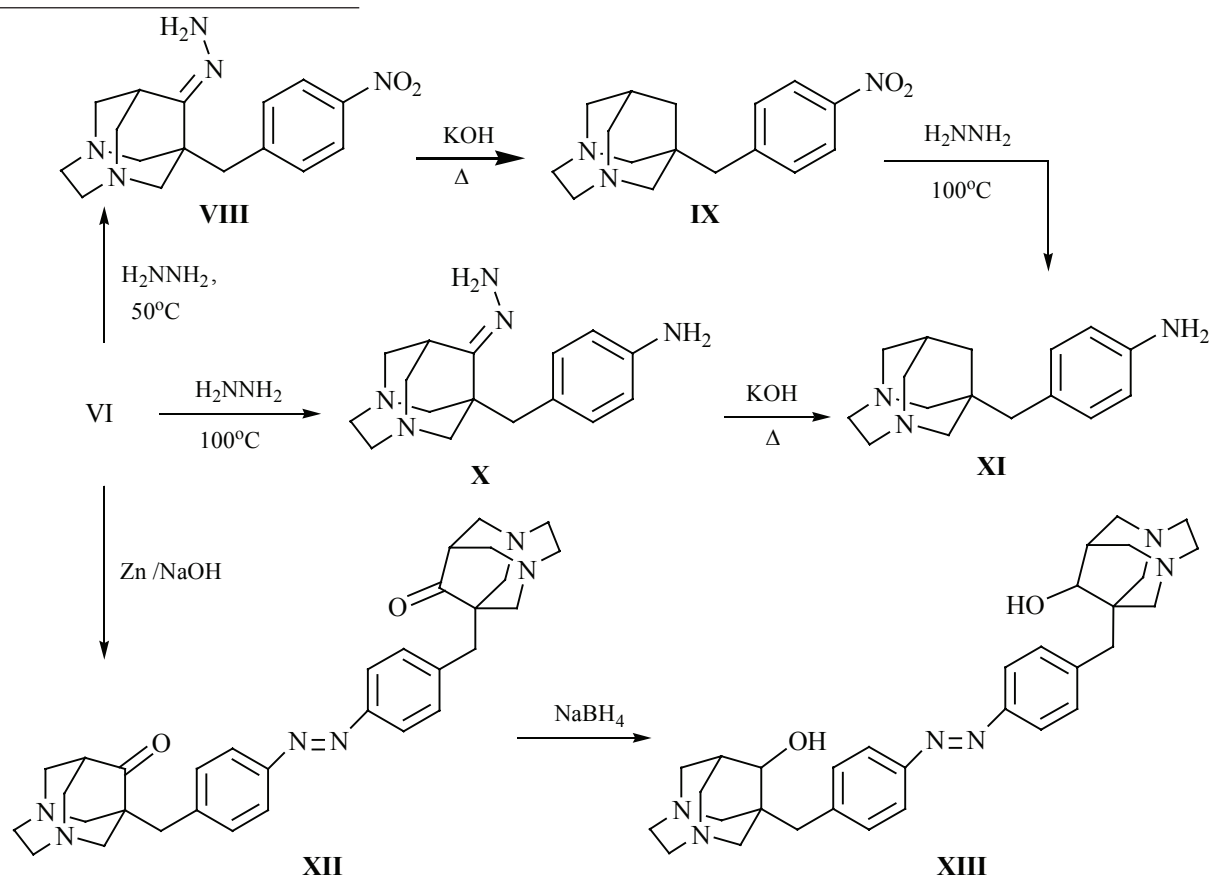
The reaction of nitroketone **VI** with hydrazine hydrate furnishes two compounds depending on the temperature. Below 50°C hydrazone of 1-(4-nitrobenzyl)-3,6-diazahomoadamantan-9-one (**VIII**) was obtained reduced by Kishner–Wolff procedure into 1-(4-nitrobenzyl)-3,6-diazahomoadamantane (**IX**). The boiling of nitroketone **VI** with hydrazine hydrate results in the noncatalytic reduction of the nitro group into amino group [6] with the formation of hydrazone of 1-(4-aminobenzyl)-3,6-diazahomoadamantan-9-one (**X**). The latter at heating

with alkali gave 4-[(3,6-diazahomoadamantan-1-yl)methyl]-aniline (**XI**) that also was formed at the noncatalytic reduction of nitrobenzyl diazohomoadamantane (**IX**) with hydrazine.

In the mass spectra of compounds **IX**, **XI** molecular ion peaks are observed as ($[M]^+$ 287) and ($[M]^+$ 257), respectively. Their main fragmentation occurs as the cleavage of the benzyl substituent and the formation of the diazohomoadamantyl cation, m/z 151.

The reduction of nitroketone **VI** with zinc and alkali in 2-propanol provided (*E*)-azobenzene-4,4'-bis{[(3,6-diazahomoadamantan-1-yl)methyl]-9-one} (**XII**), which was reduced with sodium borohydride into (*E*)-azobenzene-4,4'-bis{[1-(3,6-diazahomoadamantan-1-yl)methyl]-9-ol} (**XIII**).

The IR spectrum of compound **XII** contained absorption bands of the stretching vibrations of the carbonyl



and azo groups at 1707 and 1603 cm^{-1} , respectively, the spectrum of compound **XIII** contained two absorption bands of hydroxy groups at 3536 and 3560 cm^{-1} . In the mass spectra of compounds **XII**, **XIII** strong molecular ion peaks are observed as ($[M]^+$ 538) and ($[M]^+$ 542).

The synthesized derivatives of (*E*)-azobenzene **XII**, **XIII** under the UV-irradiation transform into *Z*-isomers and undergo the reverse conversion into *E*-isomers at heating [7]. Consequently, they may serve as molecular switches.

EXPERIMENTAL

IR spectra of the studied compounds were recorded on a spectrophotometer Bruker IFSv from pellets with KBr. ^1H NMR spectra were registered on a spectrometer Bruker WM-250 at operating frequency 250.13 MHz from solutions of compounds in CDCl_3 , internal reference TMS. Mass spectra were measured on an instrument Finnigan MAT 90 with a direct admission into the ion source, accelerating voltage 5.0 kV, cathode emission current 100 μA , ionizing electrons energy 70 eV, ionizing chamber temperature 200°C.

1-Benzyl-3,6-diazahomoadamantan-9-one (I). A mixture of 14.30 g (85 mmol) of tetramethylenediamine, 14.10 g (95 mmol) of 4-phenylbutan-2-one, and 15.30 g (260 mmol) of acetic acid in 130 mL of 2-butanol was heated for 30 min at 60–70°C. The reaction mixture was concentrated in a vacuum, the viscous residue was treated with hot heptane (4 \times 50 ml). The warm extract was purified by filtration through a bed of anhydrous aluminum oxide (10 g, II grade of activity) placed on a glass frit filter. The solvent was distilled off, the residue was recrystallized from heptane. Yield 7.00 g (32%), white crystals, mp 102–104°C. IR spectrum, ν , cm^{-1} : 1707 (C=O), 1605 (Ph). ^1H NMR spectrum, δ , ppm: 2.65 br.s (1H, CH), 2.85 s (2H, CH_2), 2.90 d (2H, NCH_2C , J 14.0 Hz), 3.00 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.15 d (2H, NCH_2C , J 14.0 Hz), 3.45 d (2H, NCH_2C , J 14.0 Hz), 7.10–7.35 m (5H, Ph). Mass spectrum, m/z (I_{rel} , %): 256 ($[M]^+$ (76), 213 (73), 165 (14), 137 (19), 131 (21), 122 (20), 101 (50), 91 (72), 72 (99), 58 (100), 43 (41). Found, %: C 74.95; H 8.05; N 10.67. $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}$. Calculated, %: C 74.96; H 7.86; N 10.92. M 256.34.

1-Benzyl-3,6-diazahomoadamantan-9-one hydrazone (II). A solution of 1.30 g (4.8 mmol) of ketone **I** in 10 mL of 80% solution of hydrazine hydrate was boiled for 3 h. The reaction mixture was evaporated, the residue

was recrystallized from toluene. Yield 1.00 g (73%), white crystals, mp 131–132°C. IR spectrum, ν , cm^{-1} : 3315, 3180 (NH_2), 1645 (C=N), 1613 (Ph). ^1H NMR spectrum, δ , ppm: 2.85 br.s (1H, CH), 2.85 s (2H, CH_2), 2.95 d (2H, NCH_2C , J 14.0 Hz), 3.00 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.10 d (2H, NCH_2C , J 14.0 Hz), 3.30 d (2H, NCH_2C , J 14.0 Hz), 5.10 br.s (2H, NH_2), 7.10–7.35 m (5H, Ph). Mass spectrum, m/z (I_{rel} , %): 270 ($[M]^+$ (32), 269 (72), 254 (43), 112 (22), 184 (22), 115 (21), 91 (52), 85 (16), 72 (100), 58 (36), 43 (41). Found, %: C 71.20; H 8.35; N 20.50. $\text{C}_{16}\text{H}_{22}\text{N}_4$. Calculated, %: C 71.07; H 8.20; N 20.72. M 270.37.

1-Benzyl-3,6-diazahomoadamantane (III). A thoroughly stirred mixture of 0.54 g (2 mmol) of hydrazone **II** and 0.60 g (11 mmol) of potassium hydroxide was heated for 2 h at 220–240°C, then cooled and extracted with toluene (3 \times 20 ml). The solvent was evaporated, the residue was recrystallized from toluene. Yield 0.30 g (62%), white crystals, mp 61–62°C. IR spectrum, ν , cm^{-1} : 1610 (Ph). ^1H NMR spectrum, δ , ppm: 1.60 s (2H, CH_2), 1.85 br.s (1H, CH), 2.35 s (2H, CH_2), 2.60 d (2H, NCH_2C , J 14.0 Hz), 2.70 d (2H, NCH_2C , J 14.0 Hz), 2.95 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.15 d (2H, NCH_2C , J 14.0 Hz), 7.10–7.15 m (5H, Ph). Mass spectrum, m/z (I_{rel} , %): 242 ($[M]^+$ (82), 198 (43), 184 (69), 151 (58), 108 (42), 91 (99), 85 (54), 73 (46), 65 (44), 57 (100), 43 (74). Found, %: C 79.15; H 9.30; N 11.30. $\text{C}_{16}\text{H}_{22}\text{N}_2$. Calculated, %: C 79.29; H 9.15; N 11.55. M 242.36.

1-Benzyl-3,6-diazahomoadamantan-9-one oxime (IV). To a solution of 1.30 g (5 mmol) of ketone **I** in 5 mL of water was added 0.42 g (6 mmol) of hydroxylamine hydrochloride. The mixture was heated at 60–70°C and at continuous stirring was added by portions within 15 min a solution of 0.62 g (6 mmol) of Na_2CO_3 in 5 mL of water. The mixture was stirred at this temperature for 10 min. The separated precipitate was filtered off, dried, and recrystallized from toluene. Yield 1.10 g (81%), white crystals, mp 236–238°C. IR spectrum, ν , cm^{-1} : 3220 (OH), 1630 (C=N), 1600 (Ph). ^1H NMR spectrum, δ , ppm: 1.89 s (2H, CH_2), 2.85 m (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.95 d (2H, NCH_2C , J 13.9 Hz), 3.02 m (2H, NCH_2C), 3.13 d (2H, NCH_2C , J 13.9 Hz), 3.30 d (2H, NCH_2C , J 13.9 Hz), 3.69 s (1H, CH), 7.10–7.15 m (2H, Ph), 7.15–7.22 m (2H, Ph), 8.75 s (1H, OH). Mass spectrum, m/z (I_{rel} , %): 271 ($[M]^+$ (100), 254 (90), 211 (31), 154 (6), 120 (5), 106 (10), 91 (14), 72 (11), 57 (13), 43 (28). Found, %: C 70.85; H 7.73; N 15.30. $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}$. Calculated, %: C 70.82; H 7.80; N 15.49. M 271.36.

1-Benzyl-3,6-diazahomoadamantan-9-amine (V).

To a slurry of 0.50 g (1.84 mmol) of oxime **IV** and 1.84 g of Ni–Al alloy (50:50) in 10 mL of water was added dropwise at vigorous stirring within 1 h a solution of 1.84 g of sodium hydroxide in 15 mL of water, maintaining the temperature of the reaction mixture below 50°C. The mixture was stirred for 2 h more, cooled, the reaction products were extracted with ether (3 × 10 mL). The ether solution was dried with potassium hydroxide and evaporated. Yield 0.38 g (81%), white crystals, mp 118–120°C. IR spectrum, ν , cm^{-1} : 3374 (NH), 1610 (Ph). ^1H NMR spectrum, δ , ppm: 1.40 s (2H, NH_2), 1.62 s (1H, CH), 2.31 d (1H, NCH_2C , J 13.9 Hz), 2.45 d (1H, NCH_2C , J 13.2 Hz), 2.49 s (1H, CH_2), 2.57 s (1H, CH_2), 2.58 d (1H, NCH_2C , J 13.2 Hz), 2.75 s (1H, CHN), 2.78 d (1H, NCH_2C , J 13.9 Hz), 2.84 d (1H, NCH_2C , J 13.9 Hz), 2.94 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.18 d (1H, NCH_2C , J 13.9 Hz), 3.38 d (1H, CHNH_2 , J 11.7 Hz), 3.53 d (1H, NCH_2C , J 13.9 Hz), 7.02–7.10 m (2H, Ph), 7.12–7.29 m (3H, Ph). Mass spectrum, m/z (I_{rel} , %): 257 [M]⁺ (100), 239 (14), 227 (12), 213 (20), 199 (39), 170 (41), 120 (10), 91 (32), 72 (69), 56 (27), 43 (36). Found, %: C 74.51; H 9.30; N 16.30. $\text{C}_{16}\text{H}_{23}\text{N}_3$. Calculated, %: C 74.67; H 9.01; N 16.33. M 257.37.

1-(4-Nitrobenzyl)-3,6-diazahomoadamantan-9-one (VI). To a solution of 0.88 g (8.7 mmol) of potassium nitrate in 18 mL of conc. H_2SO_4 cooled to 0–5°C was added at stirring with small portions within 15 min 2.20 g (8.7 mmol) of ketone **I**, the stirring without cooling was continued for 2 h, the mixture was poured into 100 mL of water and neutralized with K_2CO_3 to pH 8–9. The formed precipitate was filtered off, dried, and extracted with toluene (3 × 20 ml). The solvent was distilled off, the residue was recrystallized from toluene. Yield 1.90 g (73%), yellow crystals, mp 195–196°C. IR spectrum, ν , cm^{-1} : 1697 (C=O), 1600 (Ph), 1514, 1350 (NO_2). ^1H NMR spectrum, δ , ppm: 2.65 br.s (1H, CH), 2.85 d (2H, NCH_2C , J 14.0 Hz), 2.90 s (2H, CH_2), 3.00 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.10 d (2H, NCH_2C , J 14.0 Hz), 3.40 d (2H, NCH_2C , J 14.0 Hz), 7.25–8.20 m (4H, Ph). Mass spectrum, m/z (I_{rel} , %): 301 [M]⁺ (96), 273 (25), 258 (21), 228 (14), 128 (15), 116 (36), 106 (20), 83 (50), 72 (73), 58 (81), 42 (100). Found, %: C 63.40; H 6.49; N 13.31. $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_3$. Calculated, %: C 63.77; H 6.35; N 13.94. M 301.34.

1-(4-Aminobenzyl)-3,6-diazahomoadamantan-9-one (VII). To a solution of 0.57 g (1.9 mmol) of nitroketone **VI** in 5 mL of hydrochloric acid was added 0.5 g of tin in small granules, and the mixture was boiled for

1 h. The reaction mixture was cooled, 5 mL of water was added, and the mixture was neutralized with NaOH solution to pH 8. The reaction products were extracted with toluene (3 × 20 ml), the solvent was distilled off, the residue was recrystallized from toluene. Yield 0.35 g (69%), white crystals, mp 118–119°C. IR spectrum, ν , cm^{-1} : 3400, 3319, 3211 (NH_2), 1690 (C=O), 1612 (Ph). ^1H NMR spectrum, δ , ppm: 2.60 s (2H, CH_2), 2.70 d (2H, NCH_2C , J 14.0 Hz), 2.90 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.10 d (2H, NCH_2C , J 14.0 Hz), 3.40 d (2H, NCH_2C , J 14.0 Hz), 3.60 br.s (2H, NH_2), 3.95 br.s (1H, CH), 6.60–7.00 m (4H, Ph). Mass spectrum, m/z (I_{rel} , %): 271 [M]⁺ (29), 262 (8), 228 (12), 200 (13), 170 (5), 140 (15), 106 (35), 84 (21), 72 (100), 55 (45), 43 (41). Found, %: C 70.65; H 7.30; N 14.70. $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}$. Calculated, %: C 70.82; H 7.80; N 15.48. M 271.36.

1-(4-Nitrobenzyl)-3,6-diazahomoadamantan-9-one hydrazone (VIII). A solution of 0.60 g (2 mmol) of nitroketone **VI** in a mixture of 10 mL of 80% hydrazine hydrate and 10 mL of ethanol was heated for 3.5 h at 50°C and evaporated to dryness. The residue was recrystallized from toluene. Yield 0.35 g (56%), yellow crystals, mp 220–225°C (с разл.). IR spectrum, ν , cm^{-1} : 3309, 3181 (NH_2), 1603 (C=N), 1593 (Ph), 1513, 1343 (NO_2). ^1H NMR spectrum, δ , ppm: 2.65 br.s (1H, CH), 2.75 d (2H, NCH_2C , J 14.0 Hz), 2.90 s (2H, CH_2), 2.95 d (2H, NCH_2C , J 14.0 Hz), 3.05 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.10 d (2H, NCH_2C , J 14.0 Hz), 3.25 d (2H, NCH_2C , J 14.0 Hz), 5.10 br.s (2H, NH_2), 8.20–7.25 m (4H, C_6H_4). Mass spectrum, m/z (I_{rel} , %): 315 [M]⁺ (7), 254 (22), 211 (23), 183 (38), 168 (36), 106 (30), 101 (34), 91 (33), 72 (100), 56 (58), 43 (47). Found, %: C 59.72; H 6.91; N 22.57. $\text{C}_{16}\text{H}_{21}\text{N}_5\text{O}_2$. Calculated, %: C 60.93; H 6.71; N 22.20. M 315.37.

1-(4-Nitrobenzyl)-3,6-diazahomoadamantane (IX) was obtained similarly to compound **III** from 0.31 g (1 mmol) of hydrazone **VIII** and 0.3 g of powdered KOH. Yield 0.22 g (65%), yellow crystals, mp 141–142°C. IR spectrum, ν , cm^{-1} : 1600 (Ph), 1512, 1349 (NO_2). ^1H NMR spectrum, δ , ppm: 1.60 br.s (2H, CH_2), 1.85 br.s (1H, CH), 2.45 s (2H, CH_2), 2.60 d (2H, NCH_2C , J 14.0 Hz), 2.70 d (2H, NCH_2C , J 14.0 Hz), 2.95 d (2H, NCH_2C , J 14.0 Hz), 3.15 d (2H, NCH_2C , J 14.0 Hz), 3.20 c (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 8.20–7.20 m (4H, Ph). Mass spectrum, m/z (I_{rel} , %): 287 [M]⁺ (80), 243 (61), 229 (55), 215 (34), 151 (91), 128 (38), 95 (100), 84 (74), 72 (59), 57 (76), 42 (58). Found, %: C 70.20; H 7.69; N 14.75. $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$. Calculated,

%; C 70.81; H 7.80; N 15.48. *M* 287.36.

1-(4-Aminobenzyl)-3,6-diazahomoadamantan-9-one hydrazone (X). A solution of 0.75 g (2.5 mmol) of nitroketone VI in 10 mL of 80% hydrazine hydrate was heated for 3 h at 100°C. The reaction mixture was evaporated, the residue was recrystallized from toluene. Yield 0.6 g (85%), white crystals, mp 188–189°C. IR spectrum, ν , cm^{-1} : 3441, 3329 (NH_2), 3215 (NH_2Ph), 1632 ($\text{C}=\text{N}$), 1593 (Ph). ^1H NMR spectrum, δ , ppm: 2.35 br.s (1H, CH), 2.70 s (2H, CH_2), 2.80 d (2H, NCH_2C , J 14.0 Hz), 2.90 d (2H, NCH_2C , J 14.0 Hz), 3.00 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.15 d (2H, NCH_2C , J 14.0 Hz), 3.25 d (2H, NCH_2C , J 14.0 Hz), 3.60 br.s (2H, NH_2 Ph), 5.05 br.s (2H, NH_2), 6.60 d (2H, C_6H_4), 6.85 d (2H, C_6H_4). Mass spectrum, m/z (I_{rel} , %): 285 [M]⁺ (19), 269 (80), 197 (60), 157 (59), 130 (37), 111 (42), 106 (92), 92 (66), 72 (100), 57 (25), 42 (26). Found, %: C 67.89; H 8.59; N 23.34. $\text{C}_{16}\text{H}_{23}\text{N}_5$. Calculated, %: C 67.33; H 8.12; N 24.53. *M* 285.39.

4-[(3,6-Diazahomoadamantan-1-yl)methyl]aniline (XI). *a.* A thoroughly stirred mixture of 0.57 g (2 mmol) of hydrazone X and 0.60 g (11 mmol) of powdered potassium hydroxide was heated for 2 h 220–240°C, cooled, and extracted with toluene (3 × 20 ml). The solvent was distilled off, the residue was recrystallized from toluene. Yield 0.30 g (59%), white crystals, mp 153–154°C. IR spectrum, ν , cm^{-1} : 3338, 3177 (NH_2), 1611 (Ph). ^1H NMR spectrum, δ , ppm: 1.55 br.s (2H, CH_2), 1.80 br.s (1H, CH), 2.25 s (2H, CH_2), 2.55 d (2H, NCH_2C , J 14.0 Hz), 2.70 d (2H, NCH_2C , J 14.0 Hz), 2.90 d (2H, NCH_2C , J 14.0 Hz), 3.00 s (4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.15 d (2H, NCH_2C , J 14.0 Hz), 3.60 br.s (2H, NH_2), 6.60 d (2H, C_6H_4), 6.85 d (2H, C_6H_4). Mass spectrum, m/z (I_{rel} , %): 257 [M]⁺ (100), 213 (31), 199 (43), 185 (35), 151 (50), 106 (46), 99 (30), 82 (34), 72 (22), 57 (38), 42 (35). Found, %: C 73.95; H 9.68; N 16.37. $\text{C}_{16}\text{H}_{23}\text{N}_3$. Calculated, %: C 74.66; H 9.01; N 16.32. *M* 257.37.

b. A solution of 0.36 g (1.25 mmol) of nitrobenzyl-diazahomoadamantane (XI) in 5 mL of 80% hydrazine hydrate was boiled for 3.5 h, evaporated, the residue was sublimated in a vacuum of water-jet pump, and recrystallized from toluene. Yield 0.23 g (72%). The reaction product was identical to the substance obtained by method *a.*

(E)-Azobenzene-4,4'-bis{[(3,6-diazahomoadamantan-1-yl)methyl]-9-one} (XII). To a solution of 0.60 g (2 mmol) of nitroketone VI and 0.40 g of NaOH

in 15 mL of *i*-PrOH and 2 mL of water was added at vigorous stirring 0.80 g (20 mmol) of zinc. The reaction mixture was boiled for 3 h and on cooling the solution was decanted, evaporated, and the residue was extracted with toluene (3 × 10 ml) and recrystallized from heptane. Yield 0.53 g (88%), yellow crystals, mp 254–256°C. IR spectrum, ν , cm^{-1} : 1603 ($\text{N}=\text{N}$, Ph), 1707 ($\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.65 s (2H, 2CH), 2.89 s (4H, 2 CH_2Ph), 2.91–3.13 m (8H, 4 NCH_2C), 3.08 s (8H, 2 $\text{NCH}_2\text{CH}_2\text{N}$), 3.15 d (4H, 2 NCH_2C , J 14.3 Hz), 3.43 d (4H, 2 NCH_2C , J 13.6 Hz), 7.21–8.19 m (8H, Ph). Mass spectrum, m/z (I_{rel} , %): 538 [M]⁺ (59), 300 (26), 271 (39), 194 (11), 163 (7), 149 (8), 106 (20), 91 (39), 72 (100), 59 (29), 43 (58). Found, %: C 71.22; H 7.16; N 15.55. $\text{C}_{32}\text{H}_{38}\text{N}_6\text{O}_2$. Calculated, %: C 71.35; H 7.11; N 15.60. *M* 538.68.

(E)-Azobenzene-4,4'-bis{[(3,6-diazahomoadamantan-1-yl)methyl]-9-ol} (XIII). A solution of 0.30 g (0.6 mmol) of compound XII and 0.10 g (2.5 mmol) of NaBH_4 in 8 mL of EtOH was heated for 2 h at slight boiling. The solvent was distilled off, several drops of water was added till complete dissolution of the dry residue, water was distilled off, the residue was extracted with chloroform (4 × 40 ml). The extract was dried with MgSO_4 , evaporated, the residue was recrystallized from 2-propanol. Yield 0.53 g (88%), yellow crystals, mp 272–274°C. IR spectrum, ν , cm^{-1} : 3560, 3536 (OH), 1600 ($\text{N}=\text{N}$, Ar). Mass spectrum, m/z (I_{rel} , %): 542 [M]⁺ (100), 471 (4), 273 (32), 201 (7), 184 (19), 167 (27), 149 (12), 106 (25), 91 (17), 72 (53), 60 (33), 43 (84). Found, %: C 70.76; H 7.74; N 15.24. $\text{C}_{32}\text{H}_{42}\text{N}_6\text{O}_2$. Calculated, %: C 70.82; H 7.80; N 15.49. *M* 542.72.

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