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Organic Chemistry

Study of the Cyclization Reaction of Adamantyldiaminobenzene with Aromatic Aldehydes

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In order to synthesize new derivatives of 5(6)-(1-adamantyl)-1*H*-2R-benzimidazole, the cyclization reaction of 4-(1-adamantyl)-1,2-diaminobenzene dihydrochloride with various substituted aromatic aldehydes have been studied. Cyclization of 4-(1-adamantyl)-1,2-diaminobenzene dihydrochloride with aromatic aldehydes like as salicylic aldehyde, 5-bromsalicylic aldehyde, 3,5-dibromsalicylic aldehyde, 5-nitrosalicyl aldehyde, 3-nitrobenzaldehyde, 4-nitrobenzaldehyde, *p*-dimethylaminobenz-aldehyde, *p*-diethylaminobenzaldehyde has been conducted in absolute methanol and nitrobenzene at boiling temperature, or in acetonitrile in the presence of H_2O_2/HCl at room temperature.The reduction of synthesized nitrobenzimidazoles with molecular hydrogen to produce corresponding amines has been implemented. As a result of condensation of obtained 5(6)-(1-adamantyl)-2-(3-aminophenyl)-1*H*-benzimidazole with salicylic aldehyde and benzoyl chloride, the corresponding Schiff base and amide have been obtained. The structure of synthesized compounds has been confirmed by IR, ^{1}H, ^{13}C NMR, and mass-spectrum analysis. *© 2020 Bull. Georg. Natl. Acad. Sci.*

Adamantane, benzimidazole, adamantylbenzimidazole, condensation, cyclization

Creation of new generation of medications is still one of the keen problems in world. Searching for new means is also very important because of high drug-resistance of microorganisms and other reasons. Such unique properties are characteristic of adamantane line preparations (Amantadine, Amantol, Simmetrel, Mantadix, Rimantadine, Paramantine, Protexin, Viregite, Betsovet, Neoride, Bromantane, Kemantane etc.). They display antiviral, antimicrobial, cytotoxic, psycho-neuroimmunoregulatory and other actions simultaneously, increase energy of an organism, significantly improve emotional and physical conditions in patients, or partially enhance their biological activity [1-5].

The strategy of selection of adamantane containing benzimidazoles for our study is based on the following assumption: it is well known that

1 2 - 9

R=*o*-C_6H_4OH (**2**), 2–OH-3,5-$Br_2C_6H_2$ (**3**), 2-OH-5-Br-C_6H_3 (**4**), 2-OH-5-NO_2-C_6H_3 (**5**), 4-NO_2-C_6H_4 (**6**), 3-NO_2-C_6H_4 (**7**), *p*-$C_6H_4N(CH_3)_2$ (**8**), *p*-$C_6H_4NEt_2$ (**9**)

Scheme 1. Synthesis of 5(6)-(1-adamantyl)-1*H*-2-R-benzimidazoles (**2-9**).

Table. Synthesis of 5(6)-(1-adamantyl)-1*H*-2-R-benzimidazoles (2-9)

Entry	R	Temp (°C)	Time (h)	Solvent	Yield (%)
2	*o*-C_6H_4OH	196	3	MeOH.	83
3	2–OH-3,5-$Br_2C_6H_2$	65, 210	3	MeOH, nitrobenzene	62
4	2-OH-5-Br-C_6H_3	65, 210	2	MeOH, nitrobenzene	85
5	2-OH-5-NO_2-C_6H_3	65, 210	3,5	MeOH, nitrobenzene	70
6	4-NO_2-C_6H_4	rt	70	H_2O_2/HCl, acetonitrile	83
7	3-NO_2-C_6H_4	65, 210	9	MeOH, nitrobenzene	40
7	3-NO_2-C_6H_4	rt	100	H_2O_2/HCl, acetonitrile	96
8	*p*-$C_6H_4N(CH_3)_2$	rt	150	H_2O_2/HCl, acetonitrile	73
9	*p*-$C_6H_4NEt_2$	65, 210	3.15	MeOH, nitrobenzene	78

benzimidazoles are characterized with wide range of biological activities. Preparations created on their base are widely used in medicine, veterinary and agriculture [6-8].

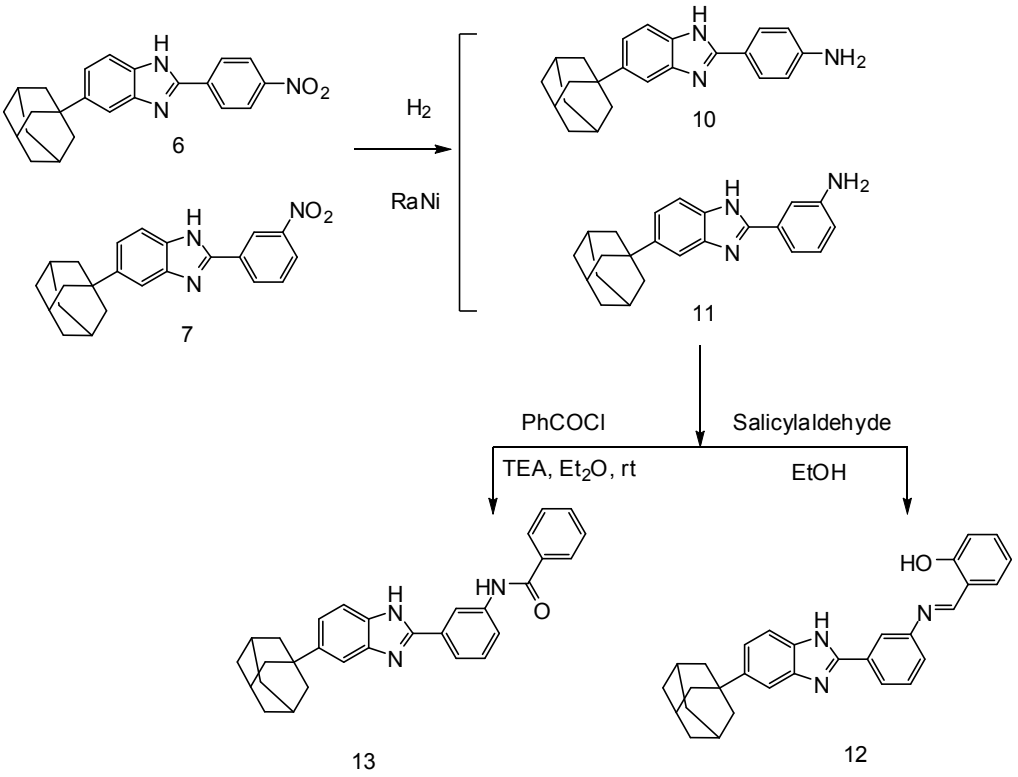
Hence, as an object of research the targeted synthesis of the prospective and actual adamantane containing benzimidazoles was selected for obtaining the new effective remedies against viral, bacterial infections and other biological agents.

Previously, we had described the synthesis and properties of 5(6)-(1-adamantyl)-1*H*-benzimidazole and 2-(1-adamantyl)-1*H*-benzimidazole derivatives [9-12]. After that our work was dedicated to the study of the cyclization reaction of 4-(1-adamantyl)-1,2-diaminobenzene dihydrochloride with some of aromatic carboxylic acids [13].

This work aims to study the cyclization reaction of 4-(1-adamantyl)-1,2-diaminobenzene dihydrochloride with some of aromatic aldehydes. The condensation reaction of 4-(1-adamantyl)-1,2-diaminobenzene (**1**) dihydrochloride with aromatic aldehydes was studied. By boiling the equimolar ratios of diaminobenzene **1** and aldehyde (salicyl-, 3,5-dibromosalicyl-, 5-bromosalicyl-, 5-nitrosalicylaldehydes, 3-nitrobenz-, 4-nitrobenz-, 4-diethylaminobenzaldehydes) in abs. alcohol and by oxidizing the obtained Schiff bases in nitrobenzene, the corresponding adamantylbenzimidazoles **2-9** were synthesized in high yields (As shown in Scheme 1 and Table).

Diaminobenzene **1** was also condensed with aldehydes at room temperature in the presence of H_2O_2/HCl in the area of acetonitrile [14]. Cyclization reaction occurred in high yield in the case of 3-nitro- and 4-nitrobenzaldehydes. In the case of 4-dimethylaminobenzaldehyde it took a long time to oxidize the resulting Schiff base to benzimidazole **9** and according to this method in

the case of 4-diethylaminobenzaldehyde only the Schiff base was obtained. Amines **10** and **11** were obtained by hydrogenation of the synthesized benzimidazoles **6** and **7** with molecular hydrogen in absolute ethanol, in the presence of Raney nickel. By interaction of amine **11** with salicylic aldehyde was synthesized Schiff base **12** and by acylation of amine **11** with benzoyl chloride in the absolute ether in the presence of triethylamine, the corresponding acylated product **13** was isolated (As shown in Scheme 2).



Scheme 2. Synthesis of 5(6)-(1-adamantyl)-1*H*-2-R-benzimidazoles **(10-13)**.

The molecular structure of the synthesized compounds was established by spectroscopy analysis, including IR, UV, ^{1}H, ^{13}C NMR and HRMS.

Experimental Part

IR spectra of the synthesized compound were recorded in the range of 400-4000 cm^{-1} with a Thermo Nicolet Avatar 370 (USA) spectrometer using Vaseline oil, hexachlorobutadiene and Varian 660 FT-IR Spectrometer using KBr pellets. UV spectra were recorded on Agilent 8453 and HP 8452 spectrometer using methanol**.** The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 and 100 MHz, respectively) using tetramethylsilane (TMS) as internal standard and Dimethylsulfoxide (DMSO-d_6) as a solvent. The high-resolution mass spectral analysis (HRMS) data were measured on a Finnigan MAT 95, CI (gas–reagent–methane). All chemicals were of reagent grade and used as commercially purchased without further purification. All reactions were monitored by thin-layer chromatography (TLC) on silica gel Al-foils and Silufol UV 254 plates using UV light and iodine as visualizing agent (if applicable), and was used as eluent CCl_4–Me_2CO, 2:1; Melting points were determined on a Boethius instrument with a PHMKO5 visual device.

5(6)-(1-Adamantyl)-2-(2-hydroxyphenyl)-1*H*-benzimidazole (2). A mixture of 4-(1-adamantyl)-1,2-diaminobenzene (1) dihydrochloride (630 mg, 2 mmol) and 0.4 mL salicyl aldehyde (488 mg, 4 mmol) was heated at 196°C for 3 h. After cooling, the reaction mixture was dissolved in hot methanol (10 mL), boiled for 15 min and after cooling 480mg of a white precipitate was isolated. An additional 250 mg of precipitate was isolated from methanol-water. The crystals were washed with hexane and dried. The white crystal of compound **2** was obtained. Yield: 83%; mp 262-264°C (MeOH), R_f 0.66. Also, this compound was obtained by the condensation of diamine **1** with salicylic acid and UV, IR, NMR and HRMS spectral date are published [13].

General procedure A) of preparation of compounds 3-5, 7, 9. A mixture of equimolar ratio of 4-(1-adamantyl)-1,2-diaminobenzene (1) dihydrochloride and aldehyde in 5-10 mL of abs. methanol was boiled for 1-3 h. To oxidize the resulting Schiff base, 3-10 mL of nitrobenzene was added to the reaction mixture and slowly heated to the boiling temperature, then the methanol and water were removed by distilling and boiled for another 5 min-8 h. The reaction progress was monitored by TLC. After cooling the reaction mixture, three times more volume of ethyl acetate was added. The precipitate was filtered and washed with hexane and dried in vacuum.

General procedure B) of preparation of compounds 6 - 8. A mixture of equimolar ratio of 4-(1-adamantyl)-1,2-diaminobenzene dihydrochloride and aldehyde in acetonitrile (15-45 mL) and 0.3-1 mL 37% HCl and 0.4-1.5 mL 45% H_2O_2 was added by dropwise. For complete oxidation of the Schiff base the mixture was stirred for 70–150 h at room t and periodically was added by 0.4-1.5 mL of 45% H_2O_2. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was diluted with water (25 mL), and with stirring 5% ammonia was added dropwise to pH 8. The precipitate was filtered off and washed with water until neutral and dried.

5(6)-(1-Adamantyl)-2-(2-hydroxy-3,5-dibromophenyl)-1*H*-benzimidazole (3). **Procedure A)** Yellow crystals of compound **3** were obtained. Yield: 62%; mp 280–281°C ($CHCl_3$). R_f 0.57 (CCl_4–Me_2CO, 10:1). Also, this compound has been obtained by the condensation of diamine **1**with 3,5-dibromosalicylic acid and UV, IR, NMR spectral data are published [13]. HRMS: m/z calculated, for $C_{23}H_{22}Br_2N_2O$: 502.0078; found: 502.0057 $[M]^+$.

5(6)-(1-Adamantyl)-2-(2-hydroxy-5-bromophenyl)-1*H*-benzimidazole (4). **Procedure A)** Cream-colored crystals of compound **4** were obtained. Yield: 85%; mp 320-322°C ($CHCl_3$). R_f0.75 (CCl_4-Me_2CO, 4:1). UV, λ max, nm (log ε): 221(4.70), 299(4.24), 306(4.34), 348(4.39). IR, (HCBD, Vaseline oil), ν, cm^{-1}**:** 3350-3200(N-H), 3302(O-H), 3050(C-H Ar), 2893, 2847(C-H Ad), 1609(C-N), 632(C-Br). ^{1}H NMR (400 MHz, ppm): δ 13.77(1H, s, NH), 9.52(1H, s, OH), 8.36(1H, d, *J*=2.4 Hz, H Ar), 7.71(1H, d, *J*=9.0 Hz, H Ar), 7.63(1H, dd,*J*=2.4, *J*=9.0 Hz, H Ar), 7.54(1H, dd,*J*=1.2, *J*=8.8 Hz, H-6), 7.17(1H, d, *J* = 8.8 Hz, H-7), 2.11-2.08(3H, m, H Ad), 1.97-1.92(6H, m, H Ad), 1.79-1.74(6H, m, H Ad).^{13}C NMR (100 MHz, ppm): δ156.57(C-OH), 148.18(1C Ar), 135.60(1C Ar), 129.98(2C Ar), 122.35(1C Ar), 120.45(1C Ar), 119.35(2C Ar), 113.89(1C Ar), 110.39(2C Ar), 109.85(1C Ar), 42.79(3C Ad), 36.03(4C Ad), 28.27(3C Ad). HRMS: m/z calculated, for $C_{23}H_{23}BrN_2O$: 424.0973; found: 424.1023 $[M]^+$.

5(6)-(1-Adamantyl)-2-(2-hydroxy-5-nitrophenyl)-1*H*-benzimidazole (5). Procedure A) Yellow-colored crystals of compound **5** were obtained. Yield 70%; mp >340°C($CHCl_3$). R_f 0.80 (CCl_4-Me_2CO, 4:1). UV, λ max, nm(log ε): 205(3.41), 297(3.06), 306(3.07), 333(3.08). IR, (HCBD,

Vaseline oil), ν, cm^{-1}**:** 3300-3200(N-H), 3271(O-H), 3094(C-H Ar), 2916, 2847(C-H Ad), 1635(CN), 1589, 1335(C-NO_2). ^{1}H NMR (400 MHz, ppm): δ 14.13(1H, s, NH), 14.12(1H, s, OH), 9.10(1H, d, *J*=2.8 Hz, H Ar), 8.23(1H, dd, *J*=2.8, *J*=9.2 Hz, H Ar), 7.65(1H, d, *J*=8.4 Hz, H-7), 7.61(1H, d, *J*=1.2 Hz, H-4), 7.42(1H, dd, *J*=1.2, *J*=8.4 Hz, H-6), 7.18(1H, d, *J*=9.2 Hz, H Ar), 2.12-2.07(3H, m, H Ad), 1.98-1.94(6H, m, H Ad), 1.79-1.74(6H, m, H Ad). ^{13}C NMR (100 MHz, ppm): δ 160.42(C-OH), 159.91(1C Ar), 154.70(1C Ar), 154.37(1C Ar), 153.12(1C Ar), 150.27(1C Ar), 147.59(1C Ar), 147.26(1C Ar), 144.14(1C Ar), 139.28(1C Ar), 134.86(1C Ar), 120.96(1C Ar), 112.85(1C Ar), 42.90(3C Ad), 36.58(1C Ad), 36.09(3C Ad), 28.31(3C Ad). HRMS: m/z calculated, for $C_{23}H_{23}N_3O_3$: 389.1739; found: 389.1738 $[M]^+$.

5(6)-(1-Adamantyl)-2-(4-nitrophenyl)-1*H*-benzimidazole (6). Procedure B) Yellow-colored crystals of compound **6** were obtained. Yield 83%; mp 299–301°C($CHCl_3$). R_f 0.87 (CCl_4-Me_2CO, 1:1). UV, λ max, nm(log ε): 207(4.51), 349(4.25). IR, (KBr), ν, cm^{-1}**:** 3551, 3327(N-H), 3105, 3071(C-H Ar), 2905, 2851(C-H Ad), 1604(CN), 1522, 1344(C-NO_2). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 12.17(1H, brs, NH), 8.37(1H, d, *J*=8.8, H Ar), 8.32(2H, d, *J*=8.6, H Ar), 8.26-8.21(2H, m, H Ar), 7.73–7.65(2H, m, H Ar), 2.28-2.25(6H, m, H Ad), 2.15-2.10(3H, m, H Ad), 1.82-1.78(6H, m, H Ad). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.70(1C Ar), 145.50(1C Ar), 143.05(1C Ar), 142.92(1C Ar), 140.08(1C Ar), 135.05(1C Ar), 133.39(1C Ar), 130.11(1C Ar), 127.27(1C Ar), 124.44(3C Ar), 109.98(1C Ar), 40.36(3C Ad), 36.72(3C Ad), 36.64(1C Ad), 29.07(3C Ad). HRMS: m/z calculated, for $C_{23}H_{23}N_3O_2$: 373.1790; found: 373.1797 $[M]^+$.

5(6)-(1-Adamantyl)–2-(3-nitrophenyl)-1*H*-benzimidazole (7). Procedure A) a) Green crystals of compound **7** were obtained. Yield 40%; mp 281-283°C ($CHCl_3$). R_f 0.65. UV Spectrum, λ max, nm (log ε): 206(5.32), 249(4.95), 313(4.07). IR spectrum, (KBr), ν, cm^{-1}: 3558, 3342, 3190(N-H), 3086(C-H Ar), 2907, 2848(C-H Ad), 1522, 1345(C-NO_2). ^{1}H NMR Spectrum (400 MHz, ppm): δ 13.13(1H, s, NH), 8.99(1H, s, H Ar), 8.58(1H, d, *J*=7.2 Hz, H Ar), 8.30 (1H, d, *J*=7.6 Hz, H Ar), 7.84(1H, t, *J*=8.0 Hz, H Ar), 7. 63(1H, s, H Ar), 7.50-7.43(1H, m, H Ar), 7.34-7.30(1H, m, H Ar), 2.13-2.01(3H, m, H Ad), 2.01-1.88(6H, m, H Ad), 1.83-1.69(6H, m, H Ad). ^{13}C NMR spectrum (100 MHz, ppm): δ 148.27(2C Ar), 132.90(1C Ar), 132.20(1C Ar), 132.17(1C Ar), 131.84(1C Ar), 131.81(1C Ar), 130.61(1C Ar), 130.55(2C Ar), 123.87(1C Ar), 120.67(1C Ar), 120.54(1C Ar), 42.94(3C Ad), 36.14(3C Ad), 35.68(1C Ad), 28.34(3C Ad). HRMS: m/z calculated, for $C_{23}H_{23}N_3O_2$: 373.1790; found: 373.1794 $[M]^+$.

b) **Procedure B)** Green crystals of compound **7** were obtained. Yield: 96%; mp 280–282°C ($CHCl_3$). R_f 0.65. HRMS: m/z calc., for $C_{23}H_{23}N_3O_2$: 373.1790; found: 373.1795 $[M]^+$.

5(6)-(1-Adamantyl)-2-(4-dimethylaminophenyl)-1*H*-benzimidazole (8). Procedure B) Cream-colored crystals of compound **8** were obtained. Yield: 73%; mp>225°C decomposes ($CHCl_3$). R_f 0.38. UV spectrum, λ max, nm(log ε): 209(4.25), 283(3.10), 325(3.85). IR spectrum, (KBr),ν, cm^{-1}: 3400, 3104(NH), 3080, 3040(C-H Ar), 2960(C-H $2CH_3$), 2903, 2847(C-H Ad), 1621(C-N). ^{1}H NMR spectrum (400 MHz, ppm): δ 12.57(1H, brs, NH), 8.23-8.00(2H, m, H Ar), 7.54-7.47(4H, m, H Ar), 7.30-7.15(1H, d,*J*=6.0, H Ar), 2.25–2.18(3H, m, H Ad), 2.07(6H, s, $2CH_3$), 1.91(6H, s, H Ad), 1.80-1.65(6H, m, H Ad). ^{13}C NMR spectrum (100 MHz, ppm): δ 154.23(1C Ar), 143.13(1C Ar), 143.12(1C Ar), 133.73(1C Ar), 121.81(1C Ar), 118.82(1C Ar), 116.17(1C Ar), 112.15(1C Ar), 109.81(1C Ar), 109.79(1C Ar), 104.96(1C Ar), 104.94(1C Ar), 103.87(1C Ar), 42.91(3C Ad), 42.85(2C $2CH_3$), 35.97(3C Ad), 35.44(1C Ad), 28.16(3C

Ad); HRMS: m/z calc., for $C_{25}H_{29}N_3$: 371.2361; Found: 371.2365 $[M]^+$.

5(6)-(1-Adamantyl)-2-(4-diethylaminophenyl)-1*H*-benzimidazole (9). Procedure A) White crystals of compound **9** were separated. Yield:78%; mp 262–264°C($CHCl_3$). R_f 0.50 (CCl_4-Me_2CO, 1:1). UV spectrum, λ max, nm(log ε): 204(3.89), 359(4.07). IR spectrum, (KBr),ν, cm^{-1}: 3401, 3209, 3152(N-H), 3047(C-H Ar), 2969(C-H Et_2), 2908, 2846(C-H Ad), 1612(C-N). ^{1}H NMR spectrum (400 MHz, ppm): δ 12.31(1H, s, NH), 7.93(2H, d, *J*=8.8 Hz, H Ar), 7.45-7.35(2H, m, H-4 and H-7), 7.17(1H, dd, *J*=1.6, *J*=8.6 Hz, H-6), 6.76(2H, d, *J*=8.8 Hz, H Ar), 3.41(4H, k, *J*=7.0 Hz, $2CH_2$), 2.11-2.05(3H, m, H Ad), 1.96-1.91(6H, m, H Ad), 1.79-1.74(6H, m, H Ad), 1.13(6H, t, *J*=7.0 Hz, $2CH_3$). ^{13}C NMR spectrum (100 MHz, ppm):δ 152.13(1C Ar) 148.26(2C Ar), 144.34(1C Ar), 127.61(3C Ar), 118.38(1C Ar), 116.58(2C Ar), 110.97(3C Ar), 43.58(2C 2-CH_2), 43.16(3C Ad), 36.21(3C Ad), 35.61(1C Ad), 28.39(3C Ad), 12.36(2C $2CH_3$). HRMS: m/z calculated, for $C_{27}H_{33}N_3$:399.2674; found: 399.2647 $[M]^+$.

5(6)-(1-Adamantyl)-2-(4-aminophenyl)-1*H*-benzimidazole (10). Compound **6** (760 mg, 2 mmol) was dissolved in abs. ethanol (100 mL) and hydrogenated with molecular hydrogen in the presence of Raney Ni, at room temp. and atm. pressure, with stirring for 8 h. The reaction mixture was filtered on a filter paper, added by abs. ethanol saturated with HCl (20-30 mL) and left overnight. The solution was evaporated, abs. ether was added and the formed precipitate was filtered, washed with abs. ether, and dried in vacuum. Cream-colored salt crystals of compound **10** were obtained. Yield: 95%; mp 221–223°C. By treating this salt with a 10% NaOH aqueous solution to pH 8–9, cream-colored crystals of compounds **10** were obtained; mp 196-198°C ($CHCl_3$). R_f 0.38. Also, this compound has been obtained by the condensation of diamine **1** with 4-aminobenzoic acid and UV, IR, NMR, HRMS spectral data are published [13].

5(6)-(1-Adamantyl)-2-(3-aminophenyl)-1*H*-benzimidazole (11). Compound **7** (1.52 g, 4 mmol) in abs. ethanol (100 mL) was hydrogenated with molecular hydrogen in the presence of Raney Ni at room temp. and atm. pressure with stirring for 24 h. The reaction mixture was filtered on a filter paper and the abs. ethanol saturated with HCl (20-30 mL) was added and left for 24 h. The solution was evaporated, abs. ether was added, and the formed precipitate was filtered, washed with abs. ether and dried in vacuum. Cream-colored crystals of compound **11** dihydrochloride were obtained. Yield: 83%; mp 243–245°C (EtOH). By treatment of this salt with a 10% NaOH solution to pH 8–9 the cream-colored crystals of compound **11** were obtained; mp 207-209°C ($CHCl_3$). R_f 0.38. Also, this compound has been obtained by the condensation of diamine **1** with 3-aminobenzoic acid and UV, IR, NMR, HRMS spectral data are published [13].

5(6)-(1-Adamantyl)-2-[3-(2-hydroxybenzylidenamino)phenyl]-1*H*-benzimidazole (12). A mixture of 5(6)-(1-adamantyl)-2-(3-aminophenyl)-1*H*-benzimidazole (**11**) (344 mg, 1 mmol) and 0.1 mL salicylic aldehyde (122 mg, 1 mmol) in abs. ethanol (25 mL) were boiled for 4 h. The reaction mixture was evaporated on a rotary evaporator to a dry residue. The residue was transferred to a Schott filter, washed with dry hexane and dried in vacuum. Yellow crystals of compound **12** were obtained. Yield 93%: mp 203–205°C. R_f 0.87. UV spectrum, λ max, nm(log ε): 228(3.53), 308(3.41). IR spectrum, (KBr), ν, cm^{-1}: 3440-3280(N-H), 3367(O-H), 3041(C-H Ar), 2904, 2848(C-H Ad), 1635(CH=N), 1608(C-N). ^{1}H NMR spectrum (400 MHz, ppm): δ 10.26(1H, s, NH), 9.21(1H, s, OH), 9.19(1H, s, CH=N), 8.59(1H, s, H Ar), 8.54(1H, s, H Ar), 8.40-8.32(1H, m, H Ar), 8.05(1H, d, *J*=6.8 Hz, H Ar), 7.93(1H, d, *J* =8.8 Hz, H Ar), 7.89-

7.61(4H, m, H Ar), 7.49-7.41(1H, m, H Ar), 7.05-7.01(1H, m, H Ar), 2.25-2.18(3H, m, H Ad), 2.15-2.07(3H, m, H Ad), 2.00-1.90(3H, m, H Ad), 1.85-1.70(6H, m, H Ad). ^{13}C NMR spectrum (100 MHz, ppm): δ 164.83(C-OH), 161.39(CH=N), 152.74(1C Ar), 149.47(1C Ar), 143.12(1C Ar), 140.16(2C Ar), 135.32(1C Ar), 132.92(1C Ar), 130.65(1C Ar), 129.78(1C Ar), 113.54(2C Ar), 42.65(3C Ad), 36.18(1C Ad), 35.96(3C Ad), 28.22(3C Ad). HRMS: m/z calculated, for $C_{30}H_{29}N_3O$: 447.2311; found: 447.2304 $[M]^+$.

5(6)-(1-Adamantyl)-2-(3-benzoylaminophenyl)-1*H*-benzimidazole (13). The solution of 5(6)-(1-adamantyl)-2-(3-aminophenyl)-1*H*-benzimidazole dihydrochloride (**11**) (420 mg, 1 mmol) in abs. ether (60 mL) was added by 0.41 mL TEA (300 mg, 3 mmol) and at room temp. by dropwise and stirring was added 0.12 mL PhCOCl (140 mg, 1 mmol) dissolved in abs. ether (10 mL). The mixture was stirred at room temp. for 6 h and left overnight. Then it was diluted with cold water (100 mL), transferred to a separator funnel, and extracted with diethyl ether. The organic phase was separated, washed with water until neutral, dried over Na_2SO_4, evaporated on a rotary evaporator. The residue was recrystallized in chloroform/hexane (1/2). White crystals of compound **13** were obtained. Yield 84%; mp 187-189°C ($CHCl_3$). R_f 0.63. Also, this compound has been obtained by the condensation of diamine **1** with 3-aminobenzoic acid and UV, IR, NMR spectral data are published [13]. HRMS: m/z calculated, for $C_{30}H_{29}N_3O$: 447.2311; found: 447.2310 $[M]^+$.

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ორგანული ქიმია

ადამანტილდიამინობენზოლის ციკლიზაციის რეაქციის შესწავლა არომატულ ალდეჰიდებთან

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5(6)-(1-ადამანტილ)-1H-2R-ბენზიმიდაზოლის ახალი წარმოებულების სინთეზის მიზნით შესწავლილია 4-(1-ადამანტილ)-1,2-დიამინობენზოლის დიჰიდროქლორიდის ციკლიზაციის რეაქცია სხვადასხვა ჩანაცვლებულ არომატულ ალდეჰიდებთან: სალიცილის ალდეჰიდი, 5-ბრომსალიცილის ალდეჰიდი, 3,5-დიბრომსალიცილის ალდეჰიდი, 5-ნიტროსალიცილის ალდეჰიდი, 3-ნიტრობენზალდეჰიდი, 4-ნიტრობენზალდეჰიდი, პ-დიმეთილამინობენზალ-დეჰიდი, პ-დიეთილამინობენზალდეჰიდი აბსოლუტური მეთანოლისა და ნიტრობენზოლის არეში დუღილის პირობებში, ან აცეტონიტრილის არეში H_2O_2/HCl თანაობისას ოთახის ტემპერატურაზე. განხორციელებულია სინთეზირებული ნიტრობენზიმიდაზოლების აღდ-გენის რეაქცია მოლეკულური წყალბადის გამოყენებით, შესაბამისი ამინების წარმოქმნით. მიღებული ამინის კონდენსაციით სალიცილის ალდეჰიდთან და ბენზოილქლორიდთან შესა-ბამისად მიღებულია შიფის ფუძე და ამიდი. სინთეზირებული ნაერთების სტრუქტურა დადასტურებულია იწ, უი, ^{1}H, ^{13}C ბმრ და მას-სპექტრების მონაცემებით.

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