

## **Synthesis of 3,5-dimethyl-1-boraadamantane and its transformation into 3,5-dimethyl-1-azaadamantane**

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All operations with lithium and organoboron compounds were carried out in an atmosphere of dry argon. The solvents were purified and distilled according to standard procedures. Both the ether and tetrahydrofuran were distilled over LiAlH<sub>4</sub> immediately prior to use. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>11</sup>B NMR spectra were recorded on Bruker AC 200P instrument (200.13 MHz for <sup>1</sup>H nuclei, 50.32 MHz for <sup>13</sup>C nuclei and 64.21 MHz for <sup>11</sup>B nuclei). <sup>1</sup>H NMR of compound **2** was obtained on Bruker AVANCE™ 600 instrument (600.13 MHz).

**Trimethylamine-3,5-dimethyl-1-boraadamantane (6)**. A solution of compound **3**<sup>7</sup> (2 g, 0.008 mol) in THF (15 ml) was placed in a flask equipped with a thermometer, a low-temperature cooler ("cooling finger" type) and a gas inlet tube, after which gaseous trimethylamine (1 g) was introduced while cooling with water. A strong heating of the reaction mass was observed. The solvent was evaporated, and the residue was recrystallized from hexane. The yield of complex **6** was 1.34 g (76%), mp. 122-122.5 °C. <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>, δ, ppm): 0.18 (br.s 4H, H-2,9), 0.39 (br.s 2H, H-2,9), 0.82 (3H, 6H, CH<sub>3</sub>), 0.94 (br.s 2H, H-4), 1.17 (br.s 4H, H-6,10), 2.89 (s, 9H, CH<sub>3</sub>N). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 33.3 (C-7), 34.7 (C-3,5), 35.5 (Me), 46.2 (C-6,10), 47.6 (CH<sub>3</sub>N), 53.8 (C-4). Found (%): C, 76.24; H, 12.50; B, 4.11; N; 6.23. Calcd for C<sub>14</sub>H<sub>28</sub>BN (%): C, 76.02; H, 12.76; B, 4.89; N; 6.33.

The substance does not change upon boiling with an equimolar amount of BF<sub>3</sub> · OEt<sub>2</sub> in hexane for 4 hours.

**3-Butyl-5,7-dimethyl-7-methylidene-3-borabicyclo[3.3.1]nonane (8)**. To a solution of compound **3**<sup>7</sup> (19.9 g, 0.085 mol) in pentane (50 ml) at -60 ° C was added dropwise 1.6 M solution <sup>n</sup>BuLi in hexane (53 ml). The reaction mixture was heated to 20 °C and stirred for 30 min. <sup>11</sup>B NMR: -20.4 (Alk<sub>4</sub>B<sup>-</sup>Li<sup>+</sup>). The solution was then cooled to 0 °C, and acetyl chloride (6.2 ml) was introduced into the flask while maintaining the temperature in the range of 0-5 ° C. The reaction mixture was stirred for 3 h at room temperature, the precipitate was filtered off, washed with

pentane (3 × 10 ml), and the solvent was removed *in vacuo*. Distillation gave 14.63 g (79%) of compound **8** as a colourless liquid susceptible for self-ignition in air, bp. 101-102 °C (2 Torr).

<sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>, δ, ppm): 0.44 (d, 1H, H(2β), <sup>2</sup>J<sub>H(2β)-H(2α)</sub>=17.7), 0.8 – 1.8 complicated spectrum of bicyclic and *n*-Bu-groups protons (18 H), 1.03 (s, 3H, 1-Me), 4.60 (br.s, =CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 14.1, 25.8 26.8, 27.8 (Bu), 32.9 (CH<sub>3</sub>), 38.4 (C-3,5), 39.2 (br. C-2,4), 50.0 (C-6,8,9), 112.2 (C=CH<sub>2</sub>), 148.8 (C(7)). <sup>11</sup>B NMR (64.21 MHz, CDCl<sub>3</sub>, δ, ppm): 79.2. Found (%): C, 82.24; H, 12.30; B, 4.21. Calcd for C<sub>15</sub>H<sub>27</sub>B (%): C, 82.57; H, 12.47; B, 4.95.

**1-Amino-3,5-dimethyladamantane - 3,5-dimethyl-1-boraadamantane (9a)**. Yield 75%. Oil. <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>, δ): 0.1 -2.2 (m, 26H, complicated multiplet of the adamantane nuclei protons), 0.79 and 0.85 (s, 6H, Me), 2.74 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (50.32 MHz, CDCl<sub>3</sub>, δ): 30.0 (Me'), 31.2 (C-8), 32.7 (C-3', 5'), 33.5 (C-7'), 35.0 (C-3, 5), 35.4 (C-Me), 40.1 (C-8, 9), 41.5 (C-2'), 42.1 (C-8', 9'), 46.3 (C -6, 10), 49.5 (C-6',10'), 50.1 (C-4'), 54.0 (C-4), 56.2 (C-1').

<sup>11</sup>B NMR (64.21 MHz, CDCl<sub>3</sub>, δ): - 5.6.

**1-Aminoadamantane - 3,5-dimethyl-1-boraadamantane (9b)**. Yield 81%, mp. 133-135 °C. <sup>1</sup>H NMR (200.13 MHz, DMSO-d<sub>6</sub>, δ): 0.3-3.4 (m, 28H, complicated multiplet of the adamantane nuclei protons), 0.90 (s, 6H, Me), 4.14 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (50.32 MHz, DMSO-d<sub>6</sub>, δ): 28.8 (C-3', 5', 7'), 30.6 (C-8), 33.0 (C-7), 34.3 (C-3,5), 35.7 (Me), 39.5 (C-4', 6', 10'), 40.0 (C-2, 9), 41.5 (C-2', 8', 9'), 46.4 (C-6, 10), 53.3 (C-4), 54.0 (C-1'). <sup>11</sup>B NMR (64.21 MHz, DMSO-d<sub>6</sub>, δ): - 5.2.

**Isoquinoline - 3,5-dimethyl-1-boraadamantane (9c)**. Yield 82%, mp 169-171 °C (decomp.). <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>, δ): 0.4 - 2.5 (m, 13H, complicated multiplet of the adamantane nuclei protons), 0.93 (s, 6H, Me), 7.7 - 8.1 (m, 5H, isoquinoline), 8.45 (s, 1H, isoquinoline), 9.12 (s, 1H, isoquinoline). <sup>13</sup>C NMR (50.32 MHz, CDCl<sub>3</sub>, δ): 31.0 (C-8), 33.7 (C-7), 34.1 (C-3,5), 35.3 (Me), 40.0 (C-3, 5), 46.4 (C-6,10), 54.1 (C-4), 122.4, 126.4, 128.1, 128.7, 128.9, 132.9, 135.9, 136.8, 147.8 (isoquinoline). <sup>11</sup>B NMR (64.21 MHz, CDCl<sub>3</sub>, δ): -3.3.

**3,5-Dimethyl-1-azoniaadamantane chloride (13)**. <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub> δ, ppm, *J*/Hz): 0.89 (s, 6H, Me), 1.48 (m, 2H. H-4), 1.53-1.75 (AB-spectrum, 4H, H-6,10, <sup>2</sup>J<sub>AB</sub> = 13.5 Hz), 2.27 (br.s., 1H. C-7), 3.01-3.15 ((AB-spectrum, 4H, H-2,9, <sup>2</sup>J<sub>AB</sub> = 13.5 Hz), 3.31 (s, 2H, H-8) . <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 26.9 (Me), 28.5 (C-7), 30.6 (C-3,5), 40.7 (C-6,10), 48.9 (C-4), 55.8 (C-8), 60.9 (C-2,9).