DOI 10.1007/s10593-016-1832-8

Chemistry of Heterocyclic Compounds **2016**, *52*(1), 21–24

Reduction of 5-(indol-3-yl)pyrrolidin-2-ones

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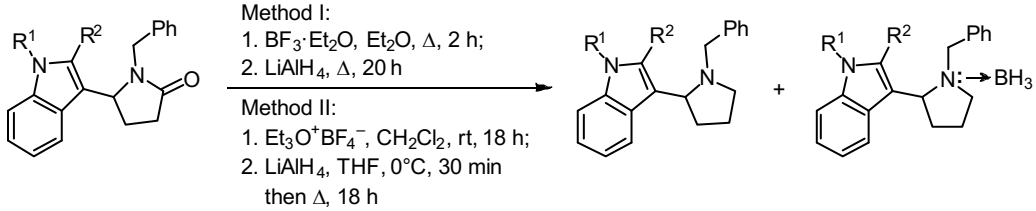
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2016, *52*(1), 21–24

Submitted December 16, 2015
Accepted January 25, 2016



The reduction of activated 5-(indol-3-yl)pyrrolidin-2-ones leading to a mixture of the respective indolyl pyrrolidines and their borane complexes, as well as several other transformations indicate that the electrophilicity of carbonyl group in 5-indolylpyrrolidin-2-ones is significantly decreased.

Keywords: 1-boryl-2-(indol-3-yl)pyrrolidinium, 2-(indol-3-yl)pyrrolidines, 5-(indol-3-yl)pyrrolidin-2-ones, reduction with complex metal hydrides.

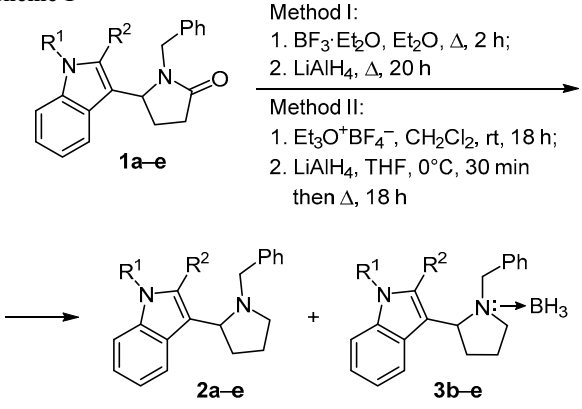
Pyrrolidine rings are found in a wide range of natural compounds: α-amino acids (proline, hydroxyproline), alkaloids (nicotine), and pharmaceuticals (piracetam, lincomycin).[1–3] No less important are indole-containing compounds, including the α-amino acid tryptophan, indole alkaloids such as vinblastine and vincristine, and pharmaceutical substances (indometacin, umifenovir).[1–3]

We have previously reported a convenient preparative method for the synthesis of 5-(indol-3-yl)- and 5-(indol-2-yl)pyrrolidones,[4] thus providing an access to these compounds for synthetic use. Pyrrolidin-2-ones are known to readily react at the carbonyl group.[5] A suppression of carbonyl group reactivity in 5-substituted pyrrolidones was observed earlier during the reduction of 1-methyl-5-phenylpyrrolidin-2-one.[6] Our attempts to use indolylpyrrolidones for analogous transformations to those possible for 5-unsubstituted pyrrolidones[5] also showed a significantly decreased reactivity of carbonyl group in the case of 5-(indol-3-yl)pyrrolidin-2-ones. We observed this phenomenon for 5-indolylpyrrolidones and their activated forms, iminium salts, during many failed attempts of pyrrolidone ring hydrolysis or hydrazinolysis as well as we noted the lack of reactivity towards organomagnesium compounds and other C-nucleophiles, that is, in the same examples where reactions with pyrrolidones occur quite readily.[5]

In all the aforementioned experiments the starting pyrrolidones were recovered nearly quantitatively, pointing to the remarkable stability of these compounds. The typical conditions for the reduction of pyrrolidones to pyrrolidines[6–8] by refluxing for 24 h with lithium aluminum hydride in THF, treating with lithium hydride, etc. (taking into account the need to preserve the indole ring) did not produce satisfactory results in the case of (indol-3-yl)-pyrrolidin-2-ones: the isolated mixtures contained the expected pyrrolidines along with the starting pyrrolidones, with the latter as major components. The presence of a labile indole moiety in the molecule limited the selection of electrophilic activating agents and prevented the use of protic acids, metal halides, and some other reagents. On the other hand, the ability of pyrrolidones to polymerize[7] prevented the use of some phosphorus and sulfur halides and even triphenylphosphine: the subsequent reduction with sodium borohydride or lithium aluminum hydride gave not only the expected pyrrolidines, but also side products: indolylpyrrolidine dimers and polymers, due to incomplete conversion of the starting pyrrolidones.

The activation of carbonyl group in compounds **1a**–**e** by complex formation with boron trifluoride allowed to prepare the target pyrrolidines **2a**–**e** only by treatment with lithium aluminum hydride (and not with sodium borohydride) (Scheme 1). In the case of compounds **1b**–**e**,

Scheme 1



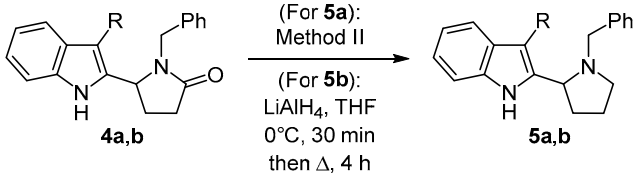
a $R^1 = R^2 = H$; **b** $R^1 = H$, $R^2 = 4\text{-MeC}_6H_4$; **c** $R^1 = Me$, $R^2 = H$; **d** $R^1 = R^2 = Me$; **e** $R^1 = Me$, $R^2 = 4\text{-MeC}_6H_4$

the isolated mixtures contained pyrrolidines **2b**–**e** and their borane complexes (compounds **3b**–**e**), formed from boron trifluoride and an excess of lithium aluminum hydride. The obtained mixtures of pyrrolidines **2b**–**e** and complexes **3b**–**e** were separated by column chromatography. It was not possible to determine the initial obtained product ratio, since the treatment of reaction mixture led to a partial decomposition of complexes **3** (according to ^{1}H NMR data, the typical ratio of complex **3** : amine **2** : pyrrolidone **1** after the work-up of reaction mixture was approximately 2 : 1 : 0.6).

The same mixture of indolylpyrrolidines **2b**–**e** and their borane complexes **3b**–**e** was obtained by activation of pyrrolidones **1b**–**e** with triethyloxonium tetrafluoroborate, followed by reduction with lithium aluminum hydride (no reduction with sodium borohydride occurred also with this method of indolylpyrrolidone activation). An exception was observed when reducing 1-benzyl-5-(indol-3-yl)-pyrrolidin-2-one (**1a**) under the same conditions, where borane complex was not formed and the reduction gave 1-benzyl-2-(indol-3-yl)pyrrolidine (**2a**) in a good yield (63%) (Scheme 1). The reduction of 1-benzyl-5-(3-methyl-indol-2-yl)pyrrolidin-2-one (**4a**) isomeric to compound **1c** under the same conditions (method II) also led to the formation of the respective pyrrolidine **5a** only (Scheme 2).

We additionally found that 1-benzyl-5-[3-(4-methyl-phenyl)indol-2-yl]pyrrolidin-2-one (**4b**) was rapidly reduced with lithium aluminum hydride without prior activation of carbonyl group with boron trifluoride or triethyloxonium tetrafluoroborate, giving a high yield of pyrrolidine **5b** (Scheme 2).

Scheme 2



a R = Me, **b** R = 4-MeC$_6$H$_4$

IR spectra of the obtained compounds lacked absorption bands due to carbonyl groups. ^{1}H NMR spectra of compounds **2a**–**e** and **5a**,**b** were in agreement with the proposed structures. All signals in the spectra of compounds **3b**–**e** were significantly shifted towards the downfield region. Mass spectra of compounds **2b**–**e** and the respective complexes **3b**–**e** were practically identical, except for additional weak signals (I_{rel} 3–5%) that were observed as expected in the spectra of borane amines **3b**–**e**, with *m*/*z* values higher by 14 units compared to the respective pyrrolidines **2b**–**e**. The structure of complex **3b** was established conclusively by X-ray structural analysis (Fig. 1).

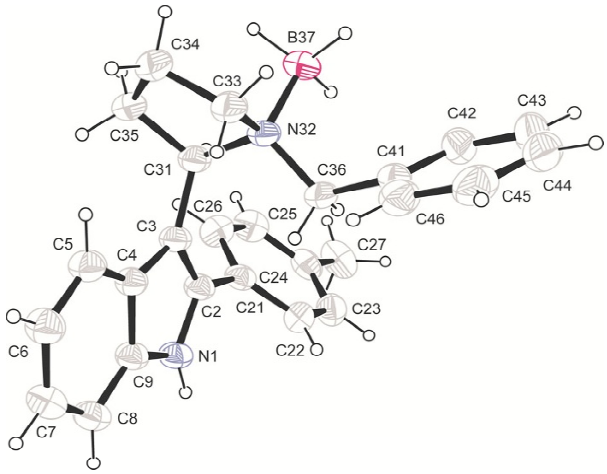


Figure 1. The structure of 1-benzyl-1-boryl-2-[2-(4-methyl-phenyl)-1*H*-indol-3-yl]pyrrolidinium (**3b**) with atoms represented by thermal vibration ellipsoids of 50% probability.

Thus, the reduction of activated 5-(indol-3-yl)pyrrolidin-2-ones to obtain a mixture of the respective indolyl pyrrolidines and their borane complexes as well as a range of other transformations provide an evidence that the electrophilicity of carbonyl group in 5-indolylpyrrolidin-2-ones is significantly suppressed. Our developed reduction methods generally were not preparative, but in some cases allowed to obtain indolylpyrrolidines in sufficiently high yields.

Experimental

IR spectra were recorded for Nujol mulls on a UR-20 instrument. ^{1}H and ^{13}C NMR spectra were acquired for $CDCl_3$ solutions on Bruker Avance-400 (400 MHz) and Agilent 400-MR (100 MHz) spectrometers, respectively, the internal standard was TMS. Mass spectra were recorded on a Bruker Autoflex II instrument, EI ionization (70 eV). Elemental analysis was performed on a Carlo Erba ER-20 CHN-analyzer. Melting points were determined on an Electrothermal IA9100 apparatus.

The reaction mixtures were separated by flash chromatography on a column with dry L grade (5/40) silica gel, the eluent was benzene. The reaction progress, column chromatography fractions, and the purity of compounds were controlled by TLC on Silufol UV-254 plates, eluent 10:1 benzene–EtOAc, visualization with iodine vapor.

The starting pyrrolidones **1a**–**e**, **4a**,**b** were synthesized according to a published procedure.[4]

Reduction of 5-indolylpyrrolidones 1a–e (General method). Method I. 5-Indolylpyrrolidone **1a–e** (0.25 mmol) was added to a refluxing solution of $BF_3 \cdot Et_2O$ (0.07 ml, 0.53 mmol) in anhydrous Et_2O (15 ml). The mixture was refluxed for 2 h, then cooled and treated by portionwise addition of $LiAlH_4$ (47 mg, 1.25 mmol), followed by refluxing of the mixture for 20 h. The reaction mixture was treated with saturated aqueous KF solution (0.8 ml), stirred for 30 min until the formation of a white precipitate of decomposition products. The ether layer was then decanted and the residue was extracted with ether. The ether extracts were combined, washed several times with water, and dried over anhydrous Na_2SO_4. Ether was removed by evaporation, the product mixture was separated by flash chromatography.

Method II. 5-Indolylpyrrolidone **1a–e** (1.0 mmol) was added to a solution of $Et_3O^+BF_4^-$ (247 mg, 1.3 mmol) in anhydrous CH_2Cl_2 (15 ml); the mixture was stirred for 3 h and left overnight at room temperature. On the next day, the reaction mixture was evaporated, the residue was dissolved in anhydrous THF (15 ml), cooled to 0°C, and treated by portionwise addition of $LiAlH_4$ (190 mg, 5.0 mmol), while maintaining the temperature at approximately 0°C. The mixture was stirred and cooled for another 30 min, then refluxed for 18 h, and worked up in the same way as in method I. The obtained product mixture was separated by flash chromatography, boranamines **3b–e** were purified by suspending in a 1:1 hexane–EtOAc mixture. Filtration of the suspension gave white crystals that were stable in air and burned with a flash when ignited.

3-(1-Benzylpyrrolidin-2-yl)-1*H*-indole (2a). Yield 63% (method I), 60% (method II), oil. IR spectrum, ν, cm^{-1}: 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.80–1.82 (1H, m) and 1.94–1.96 (1H, m, 4-CH_2); 2.04–2.06 (1H, m, 3-CH_A); 2.19–2.21 (2H, m, 3-CH_B, 5-CH_A); 3.07 (1H, d, *J* = 13.2) and 4.03 (1H, d, *J* = 13.1, C<u>H</u>$_2$Ph); 3.12–3.13 (1H, m, 5-CH_B); 3.70 (1H, dd, *J* = 8.1, *J* = 8.9, 2-CH); 7.13–7.48 (9H, m, H Ar); 7.92 (1H, d, *J* = 7.8, H Ar); 8.03 (1H, br. s, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 276 $[M]^+$ (31), 233 (14), 185 (12), 157 (38), 143 (17), 130 (25), 120 (19), 117 (35), 91 (100), 65 (20). Found, %: C 82.17; H 7.47; N 9.95. $C_{19}H_{20}N_2$. Calculated, %: C 82.57; H 7.29; N 10.14.

3-(1-Benzylpyrrolidin-2-yl)-2-(4-methylphenyl)-1*H*-indole (2b). Yield 15% (method I), 17% (method II), oil. IR spectrum, ν, cm^{-1}: 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.83–1.86 (1H, m, 4-CH_A); 2.04–2.08 (2H, m, 4-CH_B, 3-CH_A); 2.14–2.16 (1H, m) and 2.28–2.30 (1H, m, 3-CH_B, 5-CH_A); 2.47 (3H, s, ArC<u>H</u>$_3$); 2.90 (1H, d, *J* = 13.6) and 3.90 (1H, d, *J* = 13.3, C<u>H</u>$_2$Ph); 3.11–3.13 (1H, m, 5-CH_B); 3.75 (1H, dd, *J* = 7.8, *J* = 10.1, 2-CH); 7.18–7.40 (10H, m, H Ar); 7.50 (2H, d, *J* = 7.9, H Ar); 8.02 (1H, br. s, NH); 8.26 (1H, d, *J* = 7.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.3; 31.2; 44.1; 53.3; 58.2; 61.9; 110.6; 119.2; 120.4; 122.0; 127.9 (2C); 128.4 (2C); 128.7 (4C); 129.3 (2C); 136.3; 136.6. Mass spectrum, *m*/*z* (I_{rel}, %): 366 $[M(base)^*]^+$ (33), 323 (34), 275 (93), 265 (15); 247 (55), 220 (28), 207 (17), 159 (24), 91 (100), 265 (15). Found, %: C 70.44; H 6.43; N 5.86. $C_{26}H_{26}N_2 \cdot 0.5H_2B_4O_7$. Calculated, %: C 70.16; H 6.11; N 6.29.

3-(1-Benzylpyrrolidin-2-yl)-1-methyl-1*H*-indole (2c). Yield 19% (method I), 25% (method II), oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.78–1.81 (1H, m) and 1.93–1.95 (1H, m, 4-CH_2); 2.03–2.05 (1H, m, 3-CH_A); 2.17–2.21 (2H, m, 3-CH_B, 5-CH_A); 3.05 (1H, d, *J* = 13.1) and 4.03 (1H, d, *J* = 13.2, C<u>H</u>$_2$Ph); 3.11–3.13 (1H, m, 5-CH_B); 3.67 (1H, dd, *J* = 7.8, *J* = 8.1, 2-CH); 3.72 (3H, s, NCH_3); 7.06–7.08 (1H, m, H Ar); 7.12–7.38 (8H, m, H Ar); 7.90 (1H, d, *J* = 8.2, H Ar). Mass spectrum, *m*/*z* (I_{rel}, %): 290 $[M]^+$ (45), 247 (31), 199 (14), 171 (66), 157 (33), 144 (57), 91 (100), 65 (20). Found, %: C 83.09; H 7.89; N 9.17. $C_{20}H_{22}N_2$. Calculated, %: C 82.72; H 7.64; N 9.65.

3-(1-Benzylpyrrolidin-2-yl)-1,2-dimethyl-1*H*-indole (2d). Yield 18% (method I), 20% (method II), oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.82–1.84 (1H, m) and 1.98–2.02 (1H, m, 4-CH_2); 2.10–2.13 (3H, m, 3-CH_2, 5-CH_A); 2.51 (3H, s, 2-CH_3); 2.96 (1H, d, *J* = 12.9) and 3.92 (1H, d, *J* = 13.1, C<u>H</u>$_2$Ph); 3.12–3.15 (1H, m, 5-CH_B); 3.67 (1H, dd, *J* = 7.9, *J* = 10.2, 2-CH); 3.69 (3H, s, 1-CH_3); 7.12–7.30 (8H, m, H Ar); 8.00 (1H, d, *J* = 7.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 10.5; 22.2; 29.4; 31.7; 53.4; 58.2; 62.3; 99.8; 108.4; 118.5; 120.4; 126.3; 127.9 (3C); 128.7 (2C); 132.8; 136.1. Mass spectrum, *m*/*z* (I_{rel}, %): 304 $[M]^+$ (26), 225 (11), 211 (21), 185 (22), 171 (12), 160 (42), 159 (41), 120 (22), 91 (100), 65 (16). Found, %: C 82.97; H 8.14; N 9.28. $C_{21}H_{24}N_2$. Calculated, %: C 82.85; H 7.95; N 9.20.

3-(1-Benzylpyrrolidin-2-yl)-1-methyl-2-(4-methylphenyl)-1*H*-indole (2e). Yield 28% (method I), 31% (method II), oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.75–1.77 (1H, m, 4-CH_A); 1.97–2.02 (3H, m, 3-CH_2, 4-CH_B); 2.25–2.27 (1H, m) and 3.05–3.07 (1H, m, 5-CH_2); 2.50 (3H, s, ArC<u>H</u>$_3$); 2.83 (1H, d, *J* = 13.1) and 3.94 (1H, d, *J* = 13.1, C<u>H</u>$_2$Ph); 3.45 (1H, dd, *J* = 7.9, *J* = 9.8, 2-CH); 3.59 (3H, s, NCH_3); 7.16–7.38 (12H, m, H Ar); 8.26 (1H, d, *J* = 8.1, H Ar). Mass spectrum, *m*/*z* (I_{rel}, %): 380 $[M]^+$ (71), 337 (45), 289 (76), 261 (69), 234 (36), 218 (23), 159 (53), 91 (100), 65 (19). Found, %: C 84.77; H 6.94; N 6.98. $C_{27}H_{28}N_2$. Calculated, %: C 85.22; H 7.42; N 7.36.

1-Benzyl-1-boryl-2-[2-(4-methylphenyl)-1*H*-indol-3-yl]-pyrrolidinium (3b). Yield 32% (method II), mp 166–168°C (decomp.). IR spectrum: 2300–2400 cm^{-1} (B–H), 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33–1.93 (3H, m, BH_3); 2.23–2.25 (1H, m) and 2.44–2.46 (1H, m, 4-CH_2); 2.47 (3H, s, ArC<u>H</u>$_3$); 2.69–2.72 (2H, m, 3-CH_2); 3.00–3.02 (1H, m) and 3.28–3.30 (1H, m, 5-CH_2); 3.54 (1H, d, *J* = 12.1) and 3.81 (1H, d, *J* = 12.2, C<u>H</u>$_2$Ph); 5.25 (1H, dd, *J* = 8.1, *J* = 10.2, 2-CH); 7.26–7.56 (12H, m, H Ar); 7.71 (1H, d, H Ar); 8.30 (1H, br. s, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 380 $[M]^+$ (6), 366 (11), 275 (72), 247 (56), 230 (33), 220 (100), 207 (42), 159 (41), 91 (97), 65 (26).

1-Benzyl-1-boryl-2-(1-methyl-1*H*-indol-3-yl)pyrrolidinium (3c). Yield 28% (method II), mp 198–200°C. IR spectrum, ν, cm^{-1}: 2300–2400 (B–H), 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32–2.07 (3H, m, BH_3); 2.22–2.24 (2H, m, 4-CH_2); 2.64–2.66 (2H, m, 3-CH_2); 3.00–3.02 (1H, m) and 3.20–3.22 (1H, m, 5-CH_2);

* Here and below M(base) – the molar mass of the base.

3.54 (1H, d, J = 12.1) and 3.80 (1H, d, J = 12.1, C$\underline{H}_2$Ph); 3.86 (3H, s, NCH_3); 5.00 (1H, dd, J = 8.9, J = 10.1, 2-CH); 7.23–7.39 (9H, m, H Ar); 7.95 (1H, d, J = 8.1, H Ar). Mass spectrum, m/z (I_{rel}, %): 304 $[M]^+$ (4), 290 (19), 171 (38), 157 (24), 144 (100), 115 (17), 91 (77), 65 (18).

1-Benzyl-1-boryl-2-(1,2-dimethyl-1*H*-indol-3-yl)pyrrolidinium (3d). Yield 20% (method II), mp 181–182°C. IR spectrum, ν, cm^{-1}: 2300–2400 (B–H). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.30–1.87 (3H, m, BH_3); 2.31–2.34 (2H, m, 4-CH_2); 2.52–2.54 (1H, m) and 2.87–2.90 (1H, m, 3-CH_2); 2.63 (3H, s, ArC$\underline{H}_3$); 3.03–3.05 (1H, m) and 3.29–3.31 (1H, m, 5-CH_2); 3.67 (1H, d, J = 12.1) and 3.72 (1H, d, J = 12.2, C$\underline{H}_2$Ph); 3.75 (3H, s, NCH_3); 4.97–5.00 (1H, m, 2-CH); 7.24–7.40 (8H, m, H Ar); 7.59 (1H, d, J = 8.2, H Ar). Found, %: C 78.72; H 8.53; N 8.21. $C_{21}H_{27}BN_2$. Calculated, %: C 79.25; H 8.55; N 8.80.

1-Benzyl-1-boryl-2-[1-methyl-2-(4-methylphenyl)-1*H*-indol-3-yl]pyrrolidinium (3e). Yield 13% (method II), mp 163–165°C. IR spectrum, ν, cm^{-1}: 2300–2400 (B–H). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.32–1.79 (3H, m, BH_3); 2.18–2.21 (1H, m) and 2.37–2.39 (1H, m, 4-CH_2); 2.51 (3H, s, ArC$\underline{H}_3$); 2.66–2.69 (2H, m, 3-CH_2); 2.92–2.94 (1H, m) and 3.22–3.24 (1H, m, 5-CH_2); 3.55 (1H, d, J = 12.1) and 3.80 (1H, d, J = 12.1, C$\underline{H}_2$Ph); 3.59 (3H, s, NCH_3); 4.99–5.01 (1H, m, 2-CH); 7.26–7.47 (12H, m, H Ar); 7.76–7.79 (1H, m, H Ar). Mass spectrum, m/z (I_{rel}, %): 394 $[M]^+$ (9), 380 (17), 337 (21), 289 (35), 261 (40), 234 (64), 159 (28), 91 (100), 65 (20).

2-(1-Benzylpyrrolidin-2-yl)-3-methyl-1*H*-indole (5a) was obtained according to method II from 1-benzyl-5-(3-methylindol-2-yl)pyrrolidin-2-one (**4a**). Yield 59%, oil. IR spectrum, ν, cm^{-1}: 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.86–1.90 (3H, m, 3-CH_A, 4-CH_2); 2.19–2.21 (1H, m, 3-CH_B); 2.29–2.31 (1H, m) and 3.14–3.16 (1H, m, 5-CH_2); 2.36 (3H, s, CH_3); 3.20 (1H, d, J = 13.1) and 3.91 (1H, d, J = 13.2, C$\underline{H}_2$Ph); 3.80 (1H, dd, J = 7.8, J = 9.3, 2-CH); 7.06–7.08 (1H, m, H Ar); 7.17–7.36 (7H, m, H Ar); 7.57 (1H, d, J = 8.1, H Ar); 8.51 (1H, br. s, NH). Mass spectrum, m/z (I_{rel}, %): 290 $[M(base)]^+$ (27), 260 (13), 247 (83), 246 (35), 232 (27), 231 (25), 171 (27), 157 (26), 120 (49), 101 (17), 91 (100), 40 (31). Found, %: C 75.03; H 7.07; N 8.64. $C_{20}H_{22}N_2 \cdot 0.5H_3BO_3$. Calculated, %: C 74.76; H 7.37; N 8.72.

2-(1-Benzylpyrrolidin-2-yl)-3-(4-methylphenyl)-1*H*-indole (5b). A solution of 1-benzyl-5-[3-(4-methyl-phenyl)indol-2-yl]pyrrolidin-2-one (**4b**) (0.10 g, 0.26 mmol) in anhydrous THF (10 ml) was cooled with ice and treated by addition of $LiAlH_4$ (0.05 g, 1.30 mmol), while maintaining the temperature at approximately 0°C. The mixture was stirred and cooled for an additional 30 min, then refluxed for 4 h. The reaction mixture was worked up in the same way as in methods I and II, pyrrolidine **5b** was purified by chromatography. Yield 0.06 g (62%), oil. IR spectrum, ν, cm^{-1}: 3320 (N–H). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.83–1.85 (1H, m, 4-CH_A); 2.00–2.04 (2H, m, 4-CH_B, 3-CH_A); 2.25–2.29 (2H, m, 3-CH_B, 5-CH_A); 2.47 (3H, s, ArC$\underline{H}_3$); 3.11–3.17 (2H, m, 5-CH_B, C$\underline{H}_A$Ph); 3.75–3.90 (2H, m, 2_CH, C$\underline{H}_B$Ph); 7.14–7.45 (12H, m, H Ar); 7.70 (1H, d, J = 8.1, H Ar); 8.84 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.2; 29.6; 35.9; 52.9; 58.9; 60.4; 110.9; 119.1; 119.7; 121.9; 128.1 (2C); 129.2 (3C); 129.5 (4C); 131.9; 133.4; 134.6. Mass spectrum, m/z: 366 $[M]^+$. Found,%: C 79.63; H 6.45; N 7.48. $C_{26}H_{26}N_2 \cdot 0.5H_2CO_3$. Calculated, %: C 80.07; H 6.85; N 7.05.

X-ray structural analysis of compound 3b. Crystals of compound **3b** suitable for X-ray structural analysis were obtained by suspension in 1:1 hexane–EtOAc mixture. White crystals were filtered off and dried. The X-ray structural studies were performed at 295(2) K on a STOE & Cie StadiVari automated X-ray diffractometer (CuKα irradiation, λ 1.54186 Å), equipped with a DECTRIS Pilatus-100K position-sensitive detector controlled by the X-AREA software.[9] Accounting for aborption was performed with DIFABS software.[10] The structure was solved by direct methods using the SHELXS97 program.[11] The structures were refined by F^2 using the SHELXL97 program.[11] Graphical representation of molecular structure was obtained with the ORTEP-3 program.[12] The crystallographic information was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 912382).

Supplementary information files containing X-ray structural analysis data for compound **3b** are available online at http://link.springer.com/journal/10593.

This work was financially supported by the Russian Foundation for Basic Research (project 15-29-05785 ofi_m and 15-54-45051 ind_a).

NMR spectroscopy and X-ray structural analysis were partly performed on equipment paid for by the development program MGU.u67or (Agilent 400-MR spectrometer and STOE StadiVari Pilatus-100K diffractometer).

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