Ozonolysis of *ortho*-alkenylanilines

A. G. Mustafin, D. I. Dyachenko, R. R. Gataullin, G. Yu. Ishmuratov, R. Ya. Kharisov, I. B. Abdrakhmanov, and G. A. Tolstikov*

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: chemorg@anrb.ru

Ozonolysis of *N*-acyl-2-(1-methylbut-2-enyl)- and *N*-acyl-2-(cyclopent-2-enyl)anilines followed by treatment with $NaBH_4$ afforded the corresponding 2-(2-hydroxyethyl-1-methyl) and 2-(1,5-dihydroxypent-2-yl) derivatives. The reaction can be directed to indole derivatives by varying the nature of both the acyl group and reducing reagent.

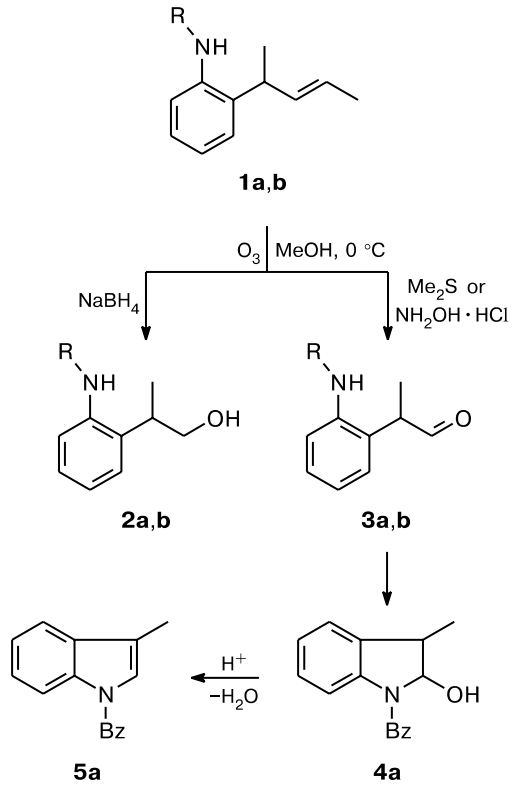
Key words: *ortho*-alkenylanilines, ozone, indoles, *N*-acetyl-2-hydroxy-3,4,4a,9a-tetrahydro-2*H*-pyrano[2,3-*b*]indole.

Alkaloids bearing oxygen-containing cyclic fragments, such as (+)-codaphniphylline,[1] deacetylisoipecoside,[2] and strychnos indole alkaloids,[3—5] have attracted considerable recent attention of researchers. Earlier, indole derivatives and compounds containing the aldehyde group have been prepared by ozonolysis of *ortho*-alkenylanilines or their *N*-trifluoroacetyl derivatives followed by treatment with Me_2S. The synthesis of indole derivatives by oxidation of *ortho*-alkenylanilines proceeds through the interaction of the newly formed carbonyl group with the amino group,[6] whereas heterocyclization in the synthesis involving *N*-trifluoroacetyl derivatives is preceded by the formation of aldehyde-containing compounds, which undergo cyclization upon the removal of the protective trifluoroacetyl group.[7] As part of our continuing studies on the use of alkenylarylamines in the synthesis of natural compounds and their analogs,[8,9] we investigated the transformations of *N*-acylated *ortho*-alkenylanilines in the course of ozonolysis.

N-Benzoyl- and *N*-acetyl-2-(1-methylbut-2-enyl)anilines (**1a** and **1b**, respectively) were oxidized by an equimolar amount of ozone in MeOH at 0 °C followed by treatment with $NaBH_4$, Me_2S, or $NH_2OH \cdot HCl$ at room temperature. Ozonization of compounds **1a**,**b** in MeOH followed by reduction with $NaBH_4$ afforded alcohols **2a**,**b**. Treatment of a reaction mixture with Me_2S or $NH_2OH \cdot HCl$ gave rise to aldehydes **3a**,**b**. Compound **3a** underwent cyclization to form 2-hydroxy-3-methylindoline (**4a**) in 81% yield upon storage for 2 days (20 °C, MeOH). The addition of catalytic amounts of TFA to compound **4a** led to dehydration of the latter giving rise to indole derivative **5a** in 84% yield (Scheme 1).

The $O_3/NaBH_4$ synthetic algorithm applied to *N*-benzoyl- and *N*-acetyl-2-(cyclopent-2-enyl)anilines (**6a** and **6b**) afforded diols **7a** and **7b**, respectively. The reactions with the use of Me_2S or $NH_2OH \cdot HCl$ proceeded, apparently, through dialdehydes **A**, which underwent cyclization to indolines **8a**,**b**. Interesting tandem cyclization was observed in the case of anilide **6b** (R = Ac) resulting in the further transformation of compound **8b** into hemiacetal **9b**[10] (Scheme 2).

Scheme 1



R = Bz (**a**), Ac (**b**)

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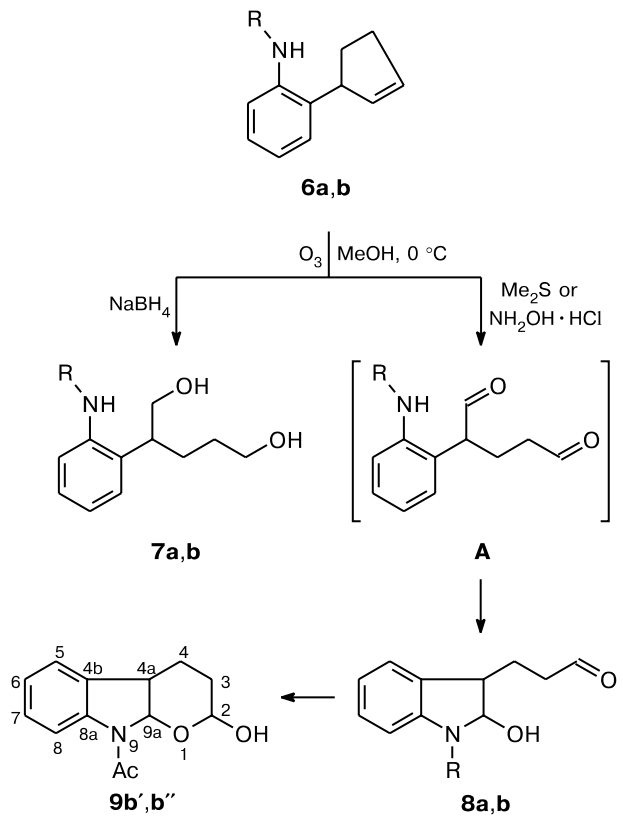
Scheme 2



R = Bz (**a**), Ac (**b**)
b′, *syn*; **b″**, *anti*

Compound **9b** was produced as two diastereomers (1 : 5), as evidenced by the fact that its ^{13}C NMR spectrum has a double number of signals of virtually all C atoms. In the ^{1}H NMR spectrum of **9b**, the signals of the protons at the C(2), C(9a), and C(4a) atoms are also doubled.

The spin-spin coupling constants of the protons at C(9a) and C(4a) for both diastereomers (5.9 and 5.3 Hz, respectively) are indicative of the *cis*-fusion of the rings at the C(9a) and C(4a) bonds.

The major diastereomer (**9b″**) gives a pseudotriplet of the acetal proton O—C<u>H</u>—OH (J = 4.9 and 4.8 Hz) in the ^{1}H NMR spectrum. In this diastereomer, the anomeric effect takes place, *i.e.*, the hydroxy group is in the axial position and in the *syn* orientation with respect to the C(9a)—N bond of the indole ring. For the minor diastereomer (**9b′**), the signal of the same proton is observed as a doublet of doublets (J = 2.3 and 9.2 Hz). The large spin-spin coupling constant indicates that the interacting protons are in the *trans*-diaxial orientations and that this minor diastereomer contains the equatorial hydroxy group. In the ^{13}C NMR spectrum, the signals of the C(2) and C(9a) atoms of major diastereomer **9b″** are observed at higher field (δ_C 91.02 and 83.13) compared to the corresponding signals of minor diastereomer **9b′** (δ_C 92.93 and 87.81). The signals of the C(2) and C(9a) atoms of the major diastereomer are observed at high field due to the 1,3-*syn* interaction between the hydroxy group and the C(9a)—N bond.[11] Consequently, the indole ring and the hydroxy group are in the *syn* and *anti* orientations in diastereomers **9b″** and diastereomer **9b′**, respectively. Hence, the diastereomers differ by the orientation of the OH group at the C(2) atom.

Therefore, the results of our study led to the conclusion that products, which hold considerable promise as biologically active compounds, can be easily prepared from readily accessible *ortho*-alkenylaniline derivatives.

Experimental

The IR spectra were measured on a UR-20 instrument (Nujol mulls). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument (300.13 MHz) in $CDCl_3$ and acetone-d_6 with Me_4Si as the internal standard. The GLC analysis was carried out on a Chrom-5 chromatograph (helium as the carried gas, 1200×3-mm column, 5% SE-30 on Chromaton N-AW-DMCS, thermal conductivity detector). Column chromatography was performed on an L 40/100 μm silica gel (Chemapol). The course of the reactions and purities of the products were monitored by TLC on Silufol UV 254 plates (Kavalier).

The solvents (benzene, hexane, MeOH, EtOH, AcOEt, $CHCl_3$, CH_2Cl_2, and Et_2O) were treated according to standard procedures.[12]

***N*-Acylation of *ortho*-alkenylanilines (general method).** Acetic anhydride or BzCl (24 mmol) was added dropwise with stirring to a solution of **2-(1-methylbut-2-enyl)-** or **2-(cyclopent-2-enyl)aniline**[13,14] (18 mmol), respectively, in anhydrous benzene (15 mL) at 0 °C. The precipitate of compound **1a**, **1b**, **6a**, or **6b** that formed was filtered off, washed with hexane (50 mL), and dried *in vacuo*.

***N*-Benzoyl-2-(1-methylbut-2-enyl)aniline (1a).** The yield was 93%, m.p. 106—107 °C (from EtOH). Found (%): C, 81.33; H, 7.02; N, 5.17. $C_{18}H_{19}NO$. Calculated (%): C, 81.51; H, 7.17; N, 5.28. IR, ν/cm^{-1}: 3250 (N—H), 1620 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.42 and 1.78 (both d, 3 H each, C(5′)H_3, C(1′)H_3, J = 7.0 Hz); 3.59 (m, 1 H, C(4′)H); 3.88 (s, 1 H, NH); 5.59 (m, 1 H, C(3′)H); 5.68 (m, 1 H, C(2′)H); 7.18—7.59 (m, 4 H, Ar); 7.80—8.28 (m, 5 H, Ar′). ^{13}C NMR, δ: 17.9 (C(1′)); 19.5 (C(5′)); 38.5 (C(4′)); 123.1 (C(6)); 125.3 (C(2′)); 125.5 (C(5)); 125.8 (C(4″)); 126.1 (C(4)); 127.1 (C(3)); 127.1 (C(6″)); 128.7 (C(3″)); 128.8 (C(7″)); 131.8 (C(5″)); 134.9 (C(2)); 135.1 (C(3″)); 135.3 (C(2″)); 135.8 (C(1)); 165.4 (C(1″)).

***N*-Acetyl-2-(1-methylbut-2-enyl)aniline (1b).** The yield was 95%, m.p. 95—98 °C (from EtOH). Found (%): C, 76.67; H, 8.29; N, 6.67. $C_{13}H_{17}NO$. Calculated (%): C, 76.85; H, 8.37; N, 6.79. IR, ν/cm^{-1}: 3220 (N—H); 1650 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.38 and 1.72 (both d, 3 H each, C(5′)H_3, C(1′)H_3, J = 7.0 Hz); 2.15 (s, 3 H, C(2″)H_3); 3.53 (m, 1 H, C(4′)H); 3.85 (s, 1 H, NH); 5.43 (m, 1 H, C(3′)H); 5.57 (m, 1 H, C(2′)H); 7.10—7.32 (m, 4 H, Ar). ^{13}C NMR, δ: 17.9 (C(1′)); 19.7 (C(5′)); 24.3 (C(2″)); 37.9 (C(4′)); 124.2 (C(6)); 124.9 (C(2′)); 125.4

(C(5)); 126.9 (C(4)); 127.0 (C(3)); 135.0 (C(2)); 135.4 (C(3′)); 135.8 (C(1)); 168.3 (C(1″)).

***N*-Benzoyl-2-(cyclopent-2-enyl)aniline (6a).** The yield was 91%, m.p. 113—115 °C (from EtOH). Found (%): C, 82.02; H, 6.24; N, 5.14. $C_{18}H_{17}NO$. Calculated (%): C, 82.13; H, 6.46; N, 5.32. IR, ν/cm^{-1}: 3280 (NH); 1630 (C=O); 780 (Ar). ^{1}H NMR ($CDCl_3$), δ: 1.82 and 2.41 (both m, 2 H each, C(5′)H$_2$, C(4′)H$_2$); 3.72 (m, 1 H, C(1′)H); 4.10 (s, 1 H, NH); 5.90 (m, 1 H, C(2′)H); 6.08 (m, 1 H, C(3′)H); 7.12—7.49 (m, 4 H, Ar); 7.84—8.23 (m, 5 H, Ar′). ^{13}C NMR, δ: 31.0 (C(5′)); 32.6 (C(4′)); 48.8 (C(1′)); 123.7 (C(6)); 125.1 (C(4)); 126.9 (C(5″)); 127.2 (C(2)); 128.5 (C(2′)); 128.7 (C(5)); 128.8 (C(3″)); 131.8 (C(7″)); 133.3 (C(3′)); 133.8 (C(3)); 134.2 (C(2″)); 134.9 (C(6″)); 135.7 (C(4″)); 135.8 (C(1)); 165.5 (C(1″)).

***N*-Acetyl-2-(cyclopent-2-enyl)aniline (6b).** The yield was 92%, m.p. 102—104 °C (from EtOH). Found (%): C, 77.40; H, 7.22; N, 6.79. $C_{13}H_{15}NO$. Calculated (%): C, 77.61; H, 7.46; N, 6.97. IR, ν/cm^{-1}: 3220 (N—H); 1660 (C=O); 770 (Ar). ^{1}H NMR ($CDCl_3$), δ: 1.70 (m, 2 H, C(5′)H$_2$); 2.12 (s, 3 H, C(2″)H$_3$); 2.45 (m, 2 H, C(4′)H$_2$); 3.68 (m, 1 H, C(1′)H); 4.02 (s, 1 H, NH); 5.88 (m, 1 H, C(2′)H); 6.02 (m, 1 H, C(3′)H); 7.05—7.38 (m, 4 H, Ar). ^{13}C NMR, δ: 24.1 (C(2″)); 31.5 (C(5′)); 32.6 (C(4′)); 47.7 (C(1′)); 124.5 (C(6)); 125.5 (C(4)); 126.8 (C(2)); 128.3 (C(2′)); 133.0 (C(5)); 133.5 (C(3′)); 135.5 (C(3)); 136.9 (C(1)); 168.7 (C(1″)).

***N*-Benzoyl-2-(2-hydroxy-1-methylethyl)aniline (2a).** An ozone-oxygen mixture was passed with stirring through a solution of compound **1a** (0.5 g, 1.9 mmol) in anhydrous MeOH (15 mL) at 0 °C until the starting compound was consumed (TLC control). The reaction mixture was purged with argon and then $NaBH_4$ (0.19 g, 5.0 mmol) was added. The mixture was stirred for 1 h, a 1 : 10 AcOH—H_2O mixture (2 mL) was added, the resulting solution was stirred for 2 h, volatile components were evaporated, and the residue was extracted with AcOEt (3×10 mL). The extract was concentrated and dried *in vacuo*. Compound **2a** was obtained in a yield of 0.48 g (94%), R_f 0.40 (95 : 5 CH_2Cl_2—MeOH as the eluent). Found (%): C, 75.17; H, 6.52; N, 5.34. $C_{16}H_{17}NO_2$. Calculated (%): C, 75.29; H, 6.67; N, 5.49. IR, ν/cm^{-1}: 3440 (OH); 3220 (NH); 1580 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.98 (d, 3 H, Me, J = 7.0 Hz); 2.88 (s, 1 H, CH); 3.30 (t, 1 H, OH, J = 9.7 Hz); 3.65 (dd, 2 H, CH_2, J = 3.4 Hz, J = 4.0 Hz); 4.85 (s, 1 H, NH); 6.91—7.43 (m, 4 H, Ar); 7.44—7.70 (m, 5 H, Ar′). ^{13}C NMR, δ: 16.3 (C(3′)); 34.7 (C(2′)); 68.7 (C(1′)); 123.1 (C(6)); 124.3 (C(4)); 124.8 (C(5)); 125.3 (C(3)); 127.0 (C(3″)); 127.5 (C(5″)); 129.1 (C(2″)); 129.8 (C(6″)); 130.7 (C(4″)); 133.9 (C(1)); 135.2 (C(1″)); 135.7 (C(2)); 163.4 (C(7″)).

***N*-Acetyl-2-(2-hydroxy-1-methylethyl)aniline (2b)** was prepared analogously from compound **1b** in a yield of 0.46 g (97%), R_f 0.35 (95 : 5 CH_2Cl_2—MeOH as the eluent). Found (%): C, 68.43; H, 7.82; N, 7.34. $C_{11}H_{15}NO_2$. Calculated (%): C, 68.39; H, 7.77; N, 7.25. IR, ν/cm^{-1}: 3480 (OH); 3260 (NH); 1560 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.13 (d, 3 H, Me, J = 7.0 Hz); 2.03 (s, 3 H, Me); 3.12 (s, 1 H, CH); 3.39 (t, 1 H, OH, J = 9.5 Hz); 3.70 (dd, 2 H, CH_2, J = 3.5 Hz, J = 4.0 Hz); 4.88 (s, 1 H, NH); 7.08—7.44 (m, 4 H, Ar). ^{13}C NMR, δ: 16.7 (C(3′)); 23.7 (C(1″)); 35.7 (C(2′)); 69.4 (C(1′)); 125.3 (C(6)); 126.2 (C(4)); 126.3 (C(5)); 126.6 (C(3)); 135.8 (C(1)); 138.0 (C(2)); 170.0 (C(2″)).

N*-Acetyl-2-(1-methyl-2-oxoethyl)aniline (3b).** ***A. An ozone-oxygen mixture was passed with stirring through a solution of compound **1b** (0.5 g, 2.5 mmol) in anhydrous MeOH (15 mL) at 0 °C until the starting compound was completely consumed (TLC control). The reaction mixture was purged with argon, Me_2S (1.6 mL) was added, volatile components were removed on a rotary evaporator, and the residue was washed with H_2O (3×10 mL). The crystals that formed were filtered off and dried *in vacuo*. Compound **3b** was obtained in a yield of 0.32 g (68%), m.p. 128—130 °C (from EtOH), R_f 0.55 (95 : 5 CH_2Cl_2—MeOH as the eluent). Found (%): C, 69.17; H, 6.89; N, 7.22. $C_{11}H_{13}NO_2$. Calculated (%): C, 69.11; H, 6.81; N, 7.33. IR, ν/cm^{-1}: 3380 (OH); 1640 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, 3 H, Me, J = 8.5 Hz); 2.38 (s, 3 H, Me); 3.13 (m, 1 H, CH); 5.23 (s, 1 H, NH); 6.98—7.27 (m, 4 H, Ar); 8.12 (s, 1 H, CH). ^{13}C NMR, δ: 20.0 (C(3′)); 23.2 (C(1″)); 40.3 (C(2′)); 116.8 (C(4)); 124.0 (C(3)); 127.6 (C(5)); 127.7 (C(1)); 130.9 (C(6)); 134.4 (C(2)); 170.5 (C(2″)); 180.1 (C(1′)).

B. An ozone-oxygen mixture was passed with stirring through a solution of compound **1b** (0.5 g, 2.5 mmol) in anhydrous MeOH (15 mL) at 0 °C until the starting compound was completely consumed (TLC control). The reaction mixture was purged with argon, $NH_2OH \cdot HCl$ (0.55 g) was added, volatile components were removed on a rotary evaporator, and the residue was washed with H_2O (3×10 mL). The crystals that formed were filtered off and dried *in vacuo*. Compound **3b** was obtained in a yield of 0.29 g (62%).

N*-Benzoyl-2-hydroxy-3-methylindoline (4a).** Compound **4a** was prepared analogously to compound **3b** (method ***A) from compound **1a** (0.5 g, 1.9 mmol) in a yield of 0.41 g (81%), R_f 0.80 (95 : 5 CH_2Cl_2—MeOH as the eluent). Found (%): C, 75.78; H, 5.81; N, 5.39. $C_{16}H_{15}NO_2$. Calculated (%): C, 75.89; H, 5.93; N, 5.53. ^{1}H NMR ($CDCl_3$), δ: 1.15 (m, 1 H, CH); 1.23 (m, 1 H, CH); 3.18 (d, 3 H, Me, J = 7.0 Hz); 5.04 (s, 1 H, OH); 7.00—7.31 (m, 4 H, Ar); 7.36—7.68 (m, 5 H, Ar′). ^{13}C NMR, δ: 19.5 (C(8)); 41.3 (C(7)); 97.3 (C(3)); 117.2 (C(6)); 124.1 (C(4)); 124.4 (C(4′)); 127.4 (C(6′)); 127.4 (C(3a)); 127.5 (C(5)); 128.3 (C(3′)); 130.5 (C(7′)); 131.7 (C(5′)); 135.9 (C(2′)); 136.2 (C(2)); 140.8 (C(7a)); 170.3 (C(1′)).

***N*-Benzoyl-3-methylindole (5a).** Trifluoroacetic acid (0.5 mL) was added to a solution of compound **4a** (0.41 g, 1.3 mmol) in $CHCl_3$ (15 mL). After 15 min, the reaction mixture was successively washed with H_2O (3×10 mL), 5% $NaHCO_3$ (3×10 mL), and again with H_2O. The solvent was removed on a rotary evaporator. The residue was recrystallized from EtOH and dried *in vacuo*. Compound **5a** was prepared in a yield of 0.37 g (84%), m.p. 83—85 °C (from EtOH), R_f 0.85 (9 : 1 CH_2Cl_2—MeOH as the eluent). Found (%): C, 81.86; H, 5.68; N, 6.12. $C_{16}H_{13}NO$. Calculated (%): C, 81.70; H, 5.53; N, 5.96. IR, ν/cm^{-1}: 1680 (C=O); 780 (Ar). ^{1}H NMR ($CDCl_3$), δ: 2.22 (s, 3 H, Me); 7.27—7.58 (m, 4 H, Ar); 7.52—7.75 (m, 5 H, Ar′); 8.33 (s, 1 H, CH). ^{13}C NMR, δ: 10.6 (C(8)); 116.5 (C(7)); 117.9 (C(3)); 118.9 (C(6)); 124.4 (C(4)); 127.1 (C(4′)); 127.5 (C(6′)); 128.4 (C(3a)); 128.7 (C(5)); 129.0 (C(3′)); 130.5 (C(7′)); 131.6 (C(5′)); 131.8 (C(2′)); 135.0 (C(2)); 136.3 (C(7a)); 168.4 (C(1′)).

***N*-Benzoyl-2-(1,5-dihydroxypent-2-yl)aniline (7a).** Compound **7a** was prepared analogously to compound **2a** from anilide **6a** (0.5 g, 1.9 mmol) in a yield of 0.39 g (70%), R_f 0.30 (9 : 1 CH_2Cl_2—MeOH as the eluent). Found (%): C, 72.43; H, 9.93; N, 4.81. $C_{18}H_{21}NO_3$. Calculated (%): C, 72.24; H, 9.72; N, 4.68. IR, ν/cm^{-1}: 3340 (OH); 3240 (NH); 1600 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.22 and 1.52 (both m, 2 H each, 2 CH_2); 2.20 (m,

1 H, CH); 2.87 (dd, 2 H, CH_2, J = 4.2 Hz, J = 5.0 Hz); 3.41 (m, 2 H, CH_2); 3.97 (dd, 2 H, 2(OH), J = 8.0 Hz, J = 8.7 Hz); 4.63 (s, 1 H, NH); 7.86—7.10 (m, 4 H, Ar); 7.02—7.21 (m, 5 H, Ar´).

***N*-Acetyl-2-(1,5-dihydroxypent-2-yl)aniline (7b).** Compound **7b** was prepared analogously to compound **7a** from anilide **6b** (0.5 g, 2.5 mmol) in a yield of 0.50 g (85%), m.p. 54—56 °C, R_f 0.30 (9 : 1 CH_2Cl_2—MeOH as eluent). Found (%): C, 66.04; H, 8.24; N, 6.12. $C_{13}H_{19}NO_3$. Calculated (%): C, 65.82; H, 8.02; N, 5.91. IR, ν/cm^{-1}: 3320 (OH); 3240 (NH); 1660 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.23 and 1.58 (both m, 2 H each, 2 CH_2); 2.13 (s, 3 H, Me); 2.27 (m, 1 H, CH); 2.95 (dd, 2 H, CH_2, J = 4.7 Hz, J = 5.7 Hz); 3.48 (m, 2H, CH_2); 4.05 (dd, 2 H, 2(OH), J = 8.0 Hz, J = 8.5 Hz); 4.72 (s, 1 H, NH); 7.05—7.33 (m, 4 H, Ar).

N*-Benzoyl-2-hydroxy-3-(3-oxopropyl)indoline (8a).** ***A. Compound **8a** was prepared analogously to compound **3b** (method ***A***) from anilide **6a** (0.5 g, 1.9 mmol) in a yield of 0.39 g (70%), m.p. 55—57 °C, R_f 0.45 (9 : 1 CH_2Cl_2—MeOH as the eluent). Found (%): C, 73.41; H, 5.92; N, 4.69. $C_{18}H_{17}NO_3$. Calculated (%): C, 73.22; H, 5.76; N, 4.75. IR, ν/cm^{-1}: 3350 (OH); 1660 (C=O); 780 (Ar). ^{1}H NMR ($CDCl_3$), δ: 1.72 and 1.98 (both m, 1 H each, C(3)H, C(4)H); 3.31 (m, 1 H, C(4a)H); 4.38 (dd, 1 H, C(2)H, J = 5.5 Hz, J = 6.7 Hz); 5.18 (d, 1 H, C(9a)H, J = 7.7 Hz); 5.80 (br.s, 1 H, OH); 7.05—7.32 (m, 4 H, Ar); 7.38—7.75 (m, 5 H, Ar). ^{13}C NMR, δ: 16.8 (C(4)); 27.6 (C(3)); 40.0 (C(4a)); 89.7 (C(9a)); 91.6 (C(2)); 118.0 (C(8)); 122.7 (C(5)); 123.9 (C(6)); 124.5 (C(3´)); 125.3 (C(7´)); 127.8 (C(7)); 128.5 (C(4´)); 128.7 (C(6´)); 130.7 (C(5´)); 133.2 (C(4b)); 135.8 (C(2´)); 142.2 (C(8a)); 169.4 (C(1´)).

B. Compound **8a** was prepared analogously to compound **3b** (method ***B***) from anilide **6a** (0.5 g, 1.9 mmol) in a yield of 0.34 g (61%).

N*-Acetyl-2-hydroxy-3,4,4a,9a-tetrahydro-2*H*-pyrano[2,3-*b*]indole (9b) (mixture of diastereomers).** ***A. Compound **9b** was prepared analogously to compound **3b** (method ***A***) from anilide **6b** (0.5 g, 2.5 mmol) in a yield of 0.49 g (85%), m.p. 136—137 °C (from EtOH), R_f 0.4 (9 : 1 CH_2Cl_2—MeOH as the eluent). Found (%): C, 67.09; H, 6.25; N, 5.73. $C_{13}H_{15}NO_3$. Calculated (%): C, 66.95; H, 6.44; N, 6.01.

B. Compound **9b** was prepared analogously to compound **3b** (method ***B***) from anilide **6b** (0.5 g 2.5 mmol) in a yield of 0.45 g (78%).

***syn*-Diastereomer (9b´).** ^{1}H NMR ($CDCl_3$), δ: 1.6 (m, 1 H, C(3)H_a); 1.83 (m, 1 H, C(3)H_b); 1.86 (m, 1 H, C(4)H_a); 2.39 (s, 3 H, C(2´)H_3); 2.40 (m, 1 H, C(4)H_b); 3.28 (m, 1 H, C(4a)H); 4.88 (dd, 1 H, C(2)H, J = 5.3 Hz, J = 9.1 Hz); 5.00 (br.s, 1 H, OH); 5.70 (d, 1 H, C(9a)H, J = 5.3 Hz); 7.05—7.24 (m, 3 H, Ar); 8.09 (d, 1 H, C(8)H, J = 7.8 Hz). ^{13}C NMR, δ: 20.6 (C(4)); 22.9 (C(2´)); 27.6 (C(3)); 38.5 (C(4a)); 87.8 (C(9a)); 92.9 (C(2)); 116.6 (C(8)); 122.5 (C(5)); 123.8 (C(6)); 127.5 (C(7)); 132.5 (C(4b)); 141.9 (C(8a)); 170.1 (C(1´)).

***anti*-Diastereomer (9b″).** ^{1}H NMR ($CDCl_3$), δ: 1.6 (m, 1 H, C(3)H_a); 1.83 (m, 1 H, C(3)H_b); 1.86 (m, 1 H, C(4)H_a); 2.31 (s, 3 H, C(2´)H_3); 2.40 (m, 1 H, C(4)H_b); 3.41 (dd, 1 H, C(4a)H, J = 7.05 Hz, J = 6.0 Hz); 4.99 (br.s, 1 H, OH); 5.20 (m, 1 H, C(2)H, J = 4.8 Hz); 5.89 (d, 1 H, C(9a)H, J = 6.0 Hz); 7.05—7.24 (m, 3 H, Ar); 8.12 (d, 1 H, C(8)H, J = 7.95 Hz). ^{13}C NMR, δ: 18.1 (C(4)); 22.8 (C(2´)); 26.7 (C(3)); 39.8 (C(4a)); 83.1 (C(9a)); 91.0 (C(2)); 116.6 (C(8)); 122.9 (C(5)); 123.9 (C(6)); 127.5 (C(7)); 132.5 (C(4b)); 142.0 (C(8a)); 170.1 (C(1´)).

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