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LETTERS TO THE EDITOR

A New Pathway of the Reaction of *N*-Acetyl-2-(2-cyclopenten-1-yl)anilines with Iodine

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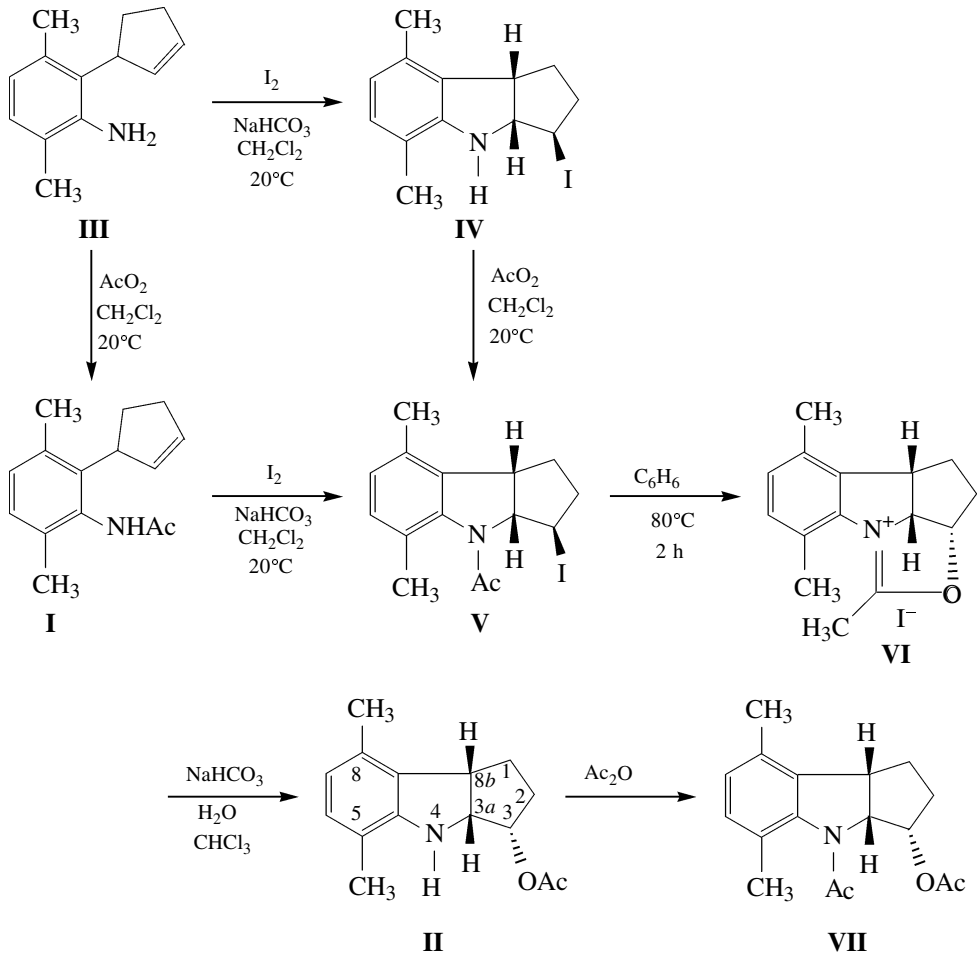
By the reaction of *N*-acetyl-2-R^1-5-R^2-6-(2-cyclopenten-1-yl)aniline with iodine in the presence of $NaHCO_3$ in CH_2Cl_2, we prepared the corresponding (3*R*,3*aR*,8*bR*)-3-acetoxy-5-R^1-8-R^2-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[b]indole.

The reaction of *o*-cycloalkenylanilines with iodine commonly yields products of either 5-*exo* or 6-*endo*-cyclization with the iodine atom outside or in the ring of the heterocyclic fragment [1]. In the reaction of acetanilide (**I**) with I_2, we unexpectedly obtained compound **II** containing no halogen. To elucide the possible mechanism of this transformation, we synthesized from cyclopentenylaniline **III** [2] 3-iodoindoline **IV**. By the subsequent acylation of **IV** we prepared its *N*-acetate (**V**), which slowly isomerizes in solution into quaternary salt **VI**. When the iodo derivative **VI** was stirred in $CHCl_3$ in the presence of water and $NaHCO_3$, it was converted into amino ester **II**. The latter reacts with Ac_2O to give diacetylated indoline **VII**. The composition and structure of the compounds obtained were determined by elemental analysis and spectroscopy.

(3*R*,3*aR*,8*bR*)-3-Acetoxy-5,8-dimethyl-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole (II). To a solution of 2.45 g of anilide **I** in 50 ml of CH_2Cl_2 we added 2.72 g of I_2 and 9 g of $NaHCO_3$. The reaction mixture was stirred at 20°C for 48 h. Then it was diluted with 150 ml of CH_2Cl_2, washed with water (3 × 50 ml), and dried over Na_2SO_4. The solvent was evaporated in a vacuum, and the product was purified to remove tarry impurities by chromatography on silica gel, eluent benzene. Yield 1.61 g (66%), mp 89–91°C (C_6H_6). IR spectrum, ν, cm^{-1}: 3375 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.60–2.05 m (4H, $2CH_2$), 2.06 s (3H, CH_3), 2.09 s (3H, CH_3), 2.20 s (3H, CH_3), 3.15 br.s (1H, NH), 3.29 d.t (1H, H^{8b}, J_1 2.6, J_2 9.0 Hz), 4.45 d.d (1H, H^{3a}, J_1 5.4, J_2 9.0 Hz), 5.05 d.t (1H, H^3, J_1 5.4, J_2 8.1 Hz), 6.45 d (1H, ArH, *J* 7.6 Hz), 6.79 d (1H, ArH, *J* 7.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.4, 18.0, 21.0, ($3CH_3$), 28.2, 20.1 (C^1, C^2), 44.5 (C^{8b}), 63.4 (C^{3a}), 77.8 (C^3), 115.3, 130.3, 130.9, 149.6 (C^{4a}, C^5, C^8, C^{8a}), 119.6, 128.5 (C^6, C^7), 171.1 (C=O). Found, %: C 73.18; H 7.57; N 5.49. $C_{15}H_{19}NO_2$. Calculated, %: C 73.44; H 7.81; N 5.71.

(3*R*,3*aR*,8*bR*)-*N*-Acetyl-3-acetoxy-5,8-dimethyl-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole (VII). To a solution of 0.44 g of heterocycle **II** in 5 ml of CH_2Cl_2 we added 0.37 g of Ac_2O; the mixture was left for 24 h. The reaction mixture was then diluted with water and extracted with 100 ml of CH_2Cl_2, the extract was washed with 5% $NaHCO_3$ until the CO_2 evolution ceased, then with water (50 ml), and dried over Na_2SO_4. After removing the solvent in a vacuum, 0.64 g of crude **VII** was obtained. By chromatography on silica gel, 0.39 g (71%) of diacetate was isolated as transparent viscous oil. R_f 0.2 (C_6H_6:EtOAc = 9:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.75–2.40 m (4H, $2CH_2$), 1.80 s (3H, CH_3), 2.15 s (3H, CH_3), 2.24 s (3H, CH_3), 2.32 s (3H, CH_3), 3.90–4.00 m (1H, H^{8b}), 4.68 d.d (1H, H^{3a}, J_1 5.6, J_2 9.5 Hz), 5.57–5.62 m (1H, H^3), 6.82 d (1H, ArH, *J* 7.6 Hz), 6.79 d (1H, ArH, *J* 7.6 Hz). ^{13}C NMR spectrum, $CDCl_3$, δ, ppm: 18.8, 20.1, 20.4, 23.1 ($4CH_3$), 29.3, 24.4 (C^1, C^2), 43.3 (C^{8b}), 67.4 (C^{3a}), 74.4 (C^3), 124.4, 130.0, 135.9, 140.6 (C^{4a}, C^5, C^8, C^{8a}), 126.2, 129.5 (C^6, C^7), 169.6, 170.0 (2C=O). Found, %: C



70.88; H 7.16; N 4.61. $C_{17}H_{21}NO_3$. Calculated, %: C 71.06; H 7.37; N 4.87.

***N*-Acetyl-3-iodo-5,8-dimethyl-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole (V).** Cyclization of 2.0 g of aniline derivative **III** was performed under the action of 2.72 g of I_2 in the presence of 9.0 g of $NaHCO_3$ similarly to the procedure for **II**. By chromatography on a short column with silica gel (eluent benzene), we obtained 2.7 g (80%) of indoline **IV** as transparent yellowish oil. R_f 0.5 (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75–1.85 m (1H, H_2^a), 1.97–2.09 m (5H, CH_3, CH_2), 2.25 s (3H, CH_3), 2.52 d.q (1H, H_2^b, J_1 4.3, J_2 9.0 Hz), 3.90 br.s (1H, NH), 3.97 d.t (1H, H^{8b}, J_1 1.0, J_2 8.6 Hz), 4.33 m (1H, H^3), 4.82 d (1H, H^{3a}, J 8.6 Hz), 6.51 d (1H, ArH, J 7.5 Hz), 6.80 d (1H, ArH, J 7.5 Hz). Found, %: C 49.93; H 5.34; I 40.36; N 4.65. $C_{13}H_{16}IN$. Calculated, %: C 49.86; H 5.15; I 40.52; N 4.47.

Heterocycle IV (0.2 g) was dissolved in 2 ml of CH_2Cl_2, and 0.1 ml of Ac_2O was added at 20°C. After 24 h, the mixture was diluted with 5 ml of H_2O, stirred for 30 min, and extracted with CH_2Cl_2 (150 ml). The extract was washed with 10% $NaHCO_3$, then with water, and dried over Na_2SO_4. After removing the solvent in a vacuum, 0.3 g of the crude product was obtained. By chromatography on a column with silica gel (3 g), 0.14 g (65%) of compound **V** was isolated as a viscous substance. R_f 0.6 (C_6H_6 : EtOAc = 9 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75–2.40 m (4H, $2CH_2$), 2.20 s (3H, CH_3), 2.25 s (3H, CH_3), 2.36 s (3H, CH_3), 4.00 t (1H, H^{8b}, J 8.0 Hz), 4.27 d.t (1H, H^3, J_1 4.0, J_2 4.7 Hz), 4.95 d.d (1H, H^{3a}, J_1 4.0, J_2 8.0 Hz), 6.83 d (1H, ArH, J 7.6 Hz), 6.95 d (1H, ArH, J 7.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.0, 20.4, 23.7 ($3CH_3$), 30.8, 31.3 (C^1, C^2), 36.2 (C^3), 44.3 (C^{8b}), 74.7 (C^{3a}), 125.6, 130.5, 134.4, 140.0 (C^{4a}, C^5, C^8, C^{8a}), 127.1, 130.1 (C^6, C^7), 170.0 (C=O). Found, %: C 50.43; H 4.78; I 35.36; N 3.67. $C_{15}H_{18}INO$. Calculated, %: C 50.72; H 5.11; I 35.73; N 3.94.

(2*aR*,4*aS*,8*cR*)-1,5,8-Trimethyl-3,4,4*a*,8*c*-tetrahydro-2*H*-2-oxa-8*b*-azoniapentaleno[1,6-*a,b*]indenium iodide (VI). Similarly to the procedure for preparing **V**, to 0.2 g of iodide **IV** we added Ac_2O. The reaction mixture was kept for 24 h, and the solvents were evaporated in a vacuum. The residue was

dissolved in benzene and refluxed for 2 h. The light yellow crystals formed in the process were filtered off. 0.16 g (80%) of compound **VI** was obtained, mp 194–196°C (benzene). ^{1}H NMR spectrum, acetone-d_6 + DMSO-d_6, δ, ppm: 1.65–2.40 m (4H, $2CH_2$), 2.00 s (3H, CH_3), 2.25 s (3H, CH_3), 2.35 s (3H, CH_3), 4.00 d.t (1H, H^{4a}, J_1 4.2, J_2 8.7 Hz), 4.75 d.d (1H, H^{8c}, J_1 5.4, J_2 8.7 Hz), 5.75 d.t (1H, H^{2a}, J_1 5.4, J_2 6.9 Hz), 7.00 d (1H, ArH, *J* 7.6 Hz), 7.05 d (1H, ArH, *J* 7.6 Hz). Found, %: C 50.47; H 4.87; I 35.38; N 3.69. $C_{15}H_{18}INO$. Calculated, %: C 50.72; H 5.11; I 35.73; N 3.94.

The IR spectra were recorded on a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer with operating frequencies of 300.13 and 75.47 MHz, respectively. Elemental analysis was performed on an M-185B C–H–N analyzer. Column chromatography was performed with silica gel Lancaster LS 40/100 μm. For qualitative TLC analysis we used Sorbfil plates (Sorbpolimer, Krasnodar, Russia), development with iodine vapor.

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