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PREPARATION OF 4,4a,9,9a-TETRAHYDRO-CARBAZOLES AND 1,3a,4,8b-TETRA-HYDROCYCLOPENTA[b]INDOLES

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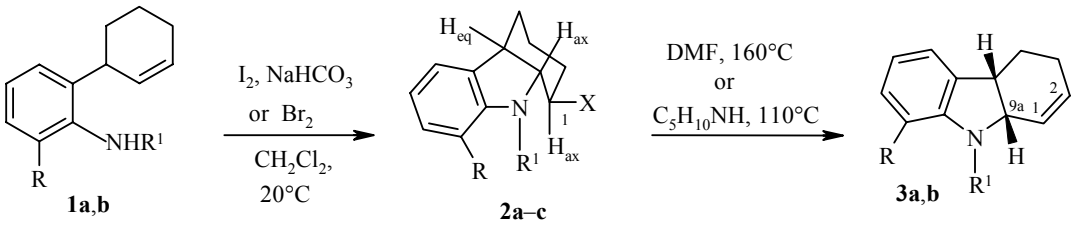
Halocyclization of mesylates or tosylates of 2-(cycloalk-2-en-1-yl)anilines gives N-methanesulfonyl- or N-toluenesulfonyl-1-halo-1,2,3,4,4a,9a-hexahydrocarbazoles, heating of which in DMF at 160°C or in piperidine at 110°C leads to 4,4a,9,9a-tetrahydro-3H-carbazoles. Heating N-methanesulfonyl-1-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole in DMF at 180-200°C gives 1,3a,4,9b-tetrahydrocyclopenta[b]indole, while in the presence of an ortho–methyl substituent the dehydroiodination reaction proceeds in piperidine at 110°C in high yield. The effect of the nature of the ortho substituent of N-methyl-1-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole on the conformational equilibrium of the cyclopentane ring has been established by ^{1}H NMR spectroscopy.

Keywords: cyclopenta[*b*]indolines, hexahydrocarbazoles, tetrahydrocarbazoles, halocyclization, dehydroiodination, conformation.

Tetrahydrocarbazoles and cyclopenta[*b*]indolines are of interest as intermediate substances in the synthesis of certain alkaloids and their analogs and have attracted the attention of a wide circle of investigators to this area of organic chemistry [1,2].

In this work we publish results of investigations on the development of new methods of synthesizing 4,4a,9,9a-tetrahydrocarbazoles and 1,3a,4,8b-tetrahydrocyclopenta[*b*]indolines by the halocyclization of 2-(cyclohex-2-en-1-yl)anilines and subsequent dehydrohalogenation of the cyclization products. Thus, the hexahydrocarbazoles **2a** [3] and **2b,c**, obtained by the halogen cyclization of anilides **1** [3] and **2**, on heating in DMF at 160°C or in piperidine at 110°C form exclusively tetrahydrocarbazoles **3a,b** with retention of the *cis* linking of the rings.



1a, **2a**,**c**, **3a** R = H, R^1 = SO_2Me, **1b–3b** R = Me, R^1 = Tos; **2 a**, **b**, X = I, **c** X = Br

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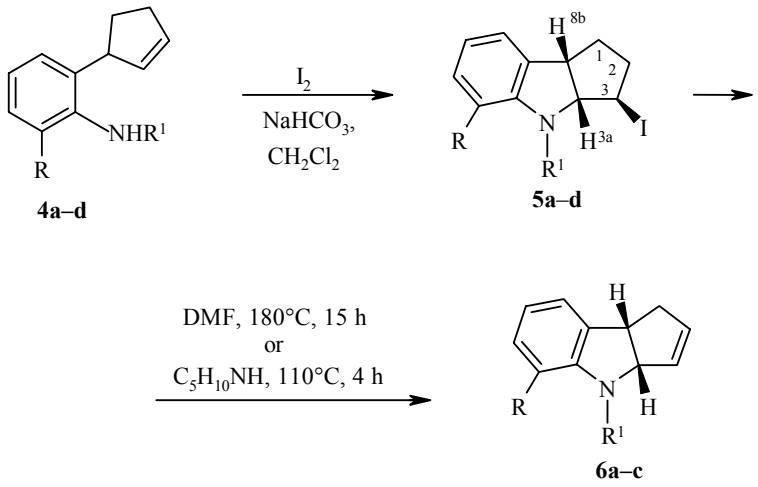
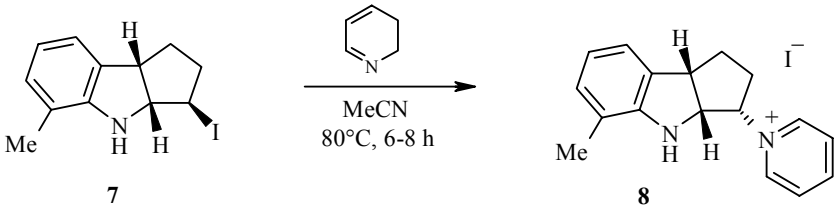
The indolines **5a-e** obtained by the iodocyclization of mesylates **4a,b** and tosylate **4c** are also subject to dehydroiodination. The dependence of the elimination conditions on the nature of the indoline *ortho* substituent was discovered in this way. Compound **5a** remains unchanged on heating in piperidine at 110°C. The expected compound **6a** was successfully obtained in high yield on carrying out the reaction in DMF at an oil bath temperature of 180-200°C for 15 h. Compounds **5b** and **5c** undergo dehydroiodination on heating in piperidine at 110°C with the formation of indolines **6b** and **6c** in good yield.



4a–d **5a–d** **6a–c**

4-6 a R = H, R^1 = SO_2Me; **b** R = Me, R^1 = SO_2Me; **c** R = Me, R^1 = Tos; **4**, **5 d** R = R^1 = H

Unlike the sulfonamides, in the absence of an amino protecting group substitution of the halogen atom occurs in cyclopenta[*b*]indole. For example, even on heating in the presence of pyridine in MeCN iodide **7** [4] gives the quaternary salt 8 in 57% yield.



7 **8**

The structures of the obtained compounds were confirmed by ^{13}C and ^{1}H NMR spectra. Two dimensional CH–CORR spectroscopy was used to correlate the carbon–proton chemical shifts. The ^{13}C NMR spectra were recorded in the JMOD mode. Assignment in the NMR spectra of the obtained compounds was carried out by the double resonance method and on the basis of the data obtained their conformational state was assessed. It was shown that hexahydrocarbazoles **2a-c** have predominantly a conformation with an equatorial disposition of halogen, shown by the large coupling constants of the $H_{(9a)}$ and $H_{(1)}$ protons [5]. Compounds **5a-c** have a *cis* linkage of rings with characteristic coupling constant $J_{H\text{-}3a,H\text{-}8b}$ = 7.8-8.6 Hz.

The dependence of the elimination conditions of indolines **5a-c** is probably linked with the different conformational states of these compounds. In compounds **5d** and **7** (described previously in [4]) the coupling constants in the ^{1}H NMR spectra of the $H_{(3)}$ proton did not exceed 2 Hz, the proton at $C_{(3)}$ occupies a pseudoequatorial position, and the conformation of the cyclopentane fragment is an envelope with pseudoaxial $C_{(3a)}$–N and $C_{(3)}$–I bonds. In compound **5a** ,with a mesyl group in the nitrogen-containing ring, $J_{H\text{-}3,Hax\text{-}2}$ is 4.6 Hz, which indicates some change in the conformation of the pentane ring compared with **7** and **5d**. The signal of the

$H_{(3)}$ proton has the form of a doublet and, on suppression of the spin-spin interaction with the 2-H_{ax} proton at δ 1.8 ppm, is transformed into a singlet. The coupling constant $J_{H\text{-}3,H\text{-}3a}$ = 0 Hz, which is possible when the torsion angle $H_{(3)}$–$C_{(3)}$–$C_{(3a)}$–$H_{(3a)}$ is close to 90°.

In the case of compound **5b**, containing substituents in the nitrogen-containing and aromatic fragments, the coupling constant of the $H_{(3)}$ and $H_{(3a)}$ protons remains at 6.0 Hz and $J_{H\text{-}3,H\text{-}2a}$ = 7.9 and $J_{H\text{-}3,H\text{-}2b}$ = 6.0 Hz are observed, i.e. the pentane ring acquires a twist form with pseudoequatorial disposition of iodine, which is probably linked with the presence of the *ortho*–methyl substituent on the phenyl ring, repelling the amino-protecting group to the side of the cyclopentane fragment. The version of the different orientation of the iodine atom in compounds **5a** and **5b** due to the difference in the mechanisms of the iodocyclization reaction of amides **4a** and **4b** is excluded, since the spectral characteristics of compound **5b**, synthesized by the iodocyclization of mesylate **4b**, were identical to the characteristics of this same compound obtained by methanesulfonation of heterocycle **7** in pyridine. The orientation of the halogen atom in amine **7** was confirmed previously by an NOE experiment [4]. Compound **5c** like compound **5b** has a substituent in the nitrogen-containing and aromatic fragments. As was to be expected the corresponding coupling constants of the $H_{(3)}$ proton also means the conformational states of these compounds are close.

It was discovered that the $H_{(4a)}$ protons in partially hydrogenated carbazoles **2a,b** and **3a,b** and analogously the $H_{(8b)}$ protons in cyclopenta[*b*]indoles **5a-c**, and **6a-c** experience different shielding depending on the nature of the substituent of the sulfonyl group, as a result of which the signal of their protons in compounds **2b, 3b, 5c,** and **6c** are displaced towards high field by approximately 0.6-0.8 ppm compared with the mesylates **2a, 3a, 5a,b**, and **6a,b**.

The multiplet signal of the $H_{(4a)}$ proton in the spectrum of tetrahydrocarbazole **3a** at 3.7 ppm, on simultaneous suppression of the spin-spin interaction with the $C_{(3)}H_2$–$C_{(4)}H_2$ protons, which have close chemical shifts, acquires the form of a doublet with coupling constant $J_{H\text{-}4a,H\text{-}9a}$ = 8.4 Hz, which confirms the retention of a *cis* linkage of the rings in the dehydrohalogenation product. The vicinal coupling constant of 10.2 Hz for the $H_{(1)}$ and $H_{(2)}$ protons of the olefin fragment at 5.9 and 6.0 ppm is characteristic for a cyclohexene ring [5]. In compounds **6a-c** the value of the analogous constant J = ~6 Hz, which is in agreement with the data for cyclopentenyl compounds [5], and the large constant between the $H_{(3a)}$ and $H_{(8b)}$ protons indicates the *cis* junction of the rings.

EXPERIMENTAL

The IR spectra were recorded on a UR 20 instrument. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 instrument (300 and 75 MHz respectively) in $CDCl_3$ (compounds **1-6**) and DMSO-d_6 (compound **8**), internal standard was TMS. Elemental analysis was carried out out on a C-H-N Analyzer M 185B instrument. Column chromatography was effected on silica gel 40/70μm (Lancaster). For qualitative TLC analysis silufol plates (Lyuminofor, Russia) were used with detection of substances by UV irradiation (λ 254 nm) or with iodine. Mass spectra were obtained on a MX 1320 spectrometer (70 eV). Melting points were determined on a Boetius stage.

N-Toluenesulfonyl-2-(cyclohex-2-en-1-yl)-6-methylaniline (1b). The reaction mixture consisting of 2-(cyclohex-2-en-1-yl)-6-methylaniline (13 mmol) and *p*-toluenesulfonyl chloride (19.5 mmol) in pyridine (15 ml) was maintained at room temperature for 24 h. Water (20 ml) was added, the mixture stirred for 30 min, and extracted with $CHCl_3$ (40 ml). The organic phase was washed with 10% aqueous $NaHCO_3$ solution, with water (20 ml), and dried over Na_2SO_4. The solvent was evaporated in vacuum, and the residue recrystallized from ethanol. Yield 90%; mp 145-147°C. IR spectrum, ν, cm^{-1}: 3290 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.2-2.1 (4H, m, $2CH_2$); 2.2 (3H, s, CH_3); 2.4 (3H, s, CH_3); 3.5 (1H, m, CH); 5.7 (2H, m, 2CH); 6.2 (1H, s, NH); 7.0-7.1 (2H, m, H-3,5); 7.1(1H, t, J = 7.0, H-4); 7.2 (2H, d, J = 8.2, H-3",5"); 7.6 (2H, d, J = 8.2, H-2",6"). Found, %: C 69.94; H 6.41; N 3.82; S 9.01. $C_{20}H_{23}NO_2S$. Calculated, %: C 70.35; H 6.79; N 4.10; S 9.39.

N-Toluenesulfonyl-1-iodo-8-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (2b). A solution of compound **1b** (5 mmol) and I_2 (10 mmol) in CH_2Cl_2 (30 ml) was maintained at room temperature, checking the progress of the reaction by TLC. After the disappearance of the starting material the mixture was diluted with CH_2Cl_2 (50 ml). The organic solution was washed with 10% $Na_2S_2O_3$ solution (60 ml), with water (2 × 20 ml), and dried over Na_2SO_4. After removing the solvent in vacuum, the residue was recrystallized from ethanol. Yield 96%; mp 215-220°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.0-2.3 (6H, m, $3CH_2$); 2.4 (3H, s, CH_3); 2.6 (3H, s, CH_3); 2.7 (1H, m, H-4a); 3.7 (1H, ddd, *J* = 4.0, *J* = 10.2, *J* = 13.5, H-1); 4.5 (1H, dd, *J* = 6.5, *J* = 10.2, H-9a); 6.8 (1H, d, *J* = 7.0, H-7); 7.1-7.2 (2H, m, H-5,6); 7.2 (2H, d, *J* = 8.1, H-3',5'); 7.5 (2H, d, *J* = 8.1, H-2',6'). Found, %: C 51.03; H 4.35; I 26.79; N 2.65; S 6.41, $C_{20}H_{22}INO_2S$. Calculated, %: C 51.40; H 4.74; I 27.15; N 3.00; S 6.86.

N-Methanesulfonyl-1-bromo-1,2,3,4,4a,9a-hexahydrocarbazole (2c). Bromine (1.25 mmol) in CH_2Cl_2 (1 ml) was added with stirring to a solution of sulfonamide **1b** (1.25 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was left for 30 min at 20°C with constant stirring. The solvent was evaporated. The obtained product was recrystallized from a mixture of $CHCl_3$–2-propanol, 7 : 3 (5 ml). The solid was filtered off. Yield 80%; mp 215-217°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.2-2.3 (6H, m, $3CH_2$); 3.1 (3H, s, CH_3); 3.8 (1H, m, H-4a); 4.0 (1H, ddd, *J* = 4.0, *J* = 8.0, *J* = 11.5, H-1); 4.5 (1H, dd, *J* = 7.7, *J* = 8.0, H-9a); 7.2-7.5 (4H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 21.2 ($C_{(3)}$); 24.0 ($C_{(4)}$); 33.9 ($C_{(2)}$); 39.3 ($C_{(4a)}$); 42.8 (CH_3); 52.1 ($C_{(1)}$); 70.8 ($C_{(9a)}$); 118.4 ($C_{(8)}$); 119.7 ($C_{(6)}$); 126.4 ($C_{(5)}$); 130.9 ($C_{(4b)}$); 137.4 ($C_{(7)}$); 140.6 ($C_{(8a)}$). Found, %: C 47.02; H 4.65; Br 23.97; N 4.01; S 9.45. $C_{13}H_{16}BrNO_2S$. Calculated, %: C 47.28; H 4.88; Br 24.20; N 4.24; S 9.71.

N-Methanesulfonyl-4,4a,9,9a-tetrahydro-3H-carbazole (3a). A solution of 1-iodohexahydrocarbazole **2a** (1.3 g) in DMF (15 ml) was heated at 160°C for 3 h [on carrying out the reaction in piperidine solution compounds **2a** or **2c** were heated in piperidine (10 ml) at 110°C for 4 h]. At the end of the dehydroiodination reaction the solvent was evaporated in vacuum, the residue was dissolved in CH_2Cl_2 (50 ml), and washed with water (2 × 20 ml). The organic phase was dried over Na_2SO_4, the solvent evaporated in vacuum, and the residue recrystallized from EtOH. Yield 98.7%; mp 111-113°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.9-2.2 (4H, m, $2CH_2$); 2.9 (3H, s, CH_3); 3.7 (1H, m, H-4a); 4.8 (1H, ddd, *J* = 1.0, *J* = 3.1, *J* = 8.4, H-9a); 5.9 (1H, ddd, *J* = 1.1, *J* = 3.1, *J* = 10.2, H-2); 6.0 (1H, ddd, *J* = 1.0, *J* = 3.3, *J* = 10.2, H-1); 7.1-7.5 (4H, m, Ar). ^{13}C NMR spectrum, δ, ppm: 20.3 ($C_{(3)}$); 23.0 ($C_{(4)}$); 36.7 (SCH_3); 38.7 ($C_{(4a)}$); 61.2 ($C_{(9a)}$); 115.1 ($C_{(8)}$); 123.6 ($C_{(6)}$); 123.7 ($C_{(5)}$); 125.2 ($C_{(1)}$); 127.7 ($C_{(2)}$); 131.7 ($C_{(7)}$); 133.8 ($C_{(4b)}$); 141.0 ($C_{(8a)}$). Found, 62.35; H 5.75; N 5.28; S 12.41. $C_{13}H_{15}NO_2S$. Calculated, %: C 62.63; H 6.06; N 5.62; S 12.86.

N-Toluenesulfonyl-8-methyl-4,4a,9,9a-tetrahydro-3H-carbazole (3b) was obtained by heating 1-iodohexahydrocarbazole **2b** (0.4 g: 0.8 mmol) in piperidine (2 ml) at 110°C for 4 h. The reaction mixture was then processed analogously to compound **3a**. Yield 98.2%; mp 168-170°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.6-1.9 (4H, m, $2CH_2$); 2.4 (3H, s, CH_3); 2.6 (3H, s, CH_3); 2.5-2.6 (1H, m, H-4a); 4.8 (1H, ddd, *J* = 1.9, *J* = 4.6, *J* = 7.0, H-9a); 5.6 (1H, dt, *J* = 2.8, *J* = 10.2, H-2); 6.0 (1H, dd, *J* = 5.0, *J* = 10.2, H-1); 6.8 (1H, d, *J* = 5.6, H-5); 7.0-7.2 (4H, m, Ar); 7.4 (2H, d, *J* = 8.2, H-2',5'). ^{13}C NMR spectrum, δ, ppm: 19.1, 21.5 ($2CH_3$); 19.8($C_{(3)}$); 21.8 ($C_{(4)}$); 37.6 ($C_{(4a)}$); 63.5 ($C_{(9a)}$); 120.1 ($C_{(8)}$); 120.5, 125.7, 126.3, 130.2, 131.1 ($C_{(5)}$, $C_{(6)}$, $C_{(7)}$, $C_{(1)}$, $C_{(2)}$); 127.4 ($C_{(6')}$, $C_{(2')}$); 129.3 ($C_{(3')}$, $C_{(5')}$); 127.7, 133.3, 135.2, 138.7, 143.7 ($C_{(4b)}$, $C_{(8)}$, $C_{(8a)}$, $C_{(1)}$, $C_{(4')}$). Found, %: C 50.98; H 4.43; I 26.76; N 2.71; S 6.43. $C_{20}H_{22}INO_2S$. Calculated, %: C 51.40; H 4.74; I 27.15; N 3.00; S 6.86.

N-Methanesulfonyl-2-(cyclopent-2-en-1-yl)aniline (4a). The reaction mixture consisting of 2-(cyclopent-2-en-1-yl)aniline (33 mmol) and methanesulfonyl chloride (49.5 mmol) in pyridine (15 ml) was maintained at room temperature for 24 h. At the end of the reaction the pyridine was evaporated in vacuum, the residue was dissolved in CH_2Cl_2 (50 ml), washed with 10% aqueous $NaHCO_3$ solution (20 ml), with water (2 × 20 ml), and dried over Na_2SO_4. The solvent was evaporated in vacuum. The yield of viscous orange oil was 93.6%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.6-1.8 (1H, m, CH); 2.4-2.7 (3H, m, CH_2, CH); 3.0 (3H, s, CH_3); 4.0-4.2 (1H, m, CH); 5.7-5.8 (1H, m, HC=C); 6.0-6.1 (1H, m, C=CH); 6.7 (1H, br s, NH); 7.1-7.3 (3H, m, H Ar); 7.5 (1H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum, δ, ppm: 32.3, 32.4 ($2CH_2$); 39.7 (CH_3); 46.3 ($C_{(1')}$); 123.3 ($C_{(4)}$); 126.2 ($C_{(6)}$); 127.0 ($C_{(5)}$); 128.5 ($C_{(1')}$); 132.9 ($C_{(3)}$); 133.2 ($C_{(2')}$); 133.9 ($C_{(2)}$); 138.8 ($C_{(1)}$). Found, %: C 60.19; H 5.95; N 5.23; S 13.03. $C_{12}H_{15}NO_2S$. Calculated, %: C 60.73; H 6.37; N 5.90; S 13.51.

N-Methanesulfonyl-2-(cyclopent-2-en-1-yl)-6-methylaniline (4b) was obtained analogously to compound **4a** from 2-(cyclopent-2-en-1-yl)-6-methylaniline (3 mmol) and methanesulfonyl chloride (4.5 mmol). After chromatography through a thin layer of silica gel (eluent CCl_4) yield 89%; mp 115-116°C, R_f 0.2 (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 3290 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.6-1.7 (2H, m, CH_2); 2.1 (3H, s, CH_3); 2.4-2.5 (2H, m, CH_2); 3.0 (3H, s, SCH_3); 4.4 (1H, m, H-1'); 5.7 (1H, m, H-2'); 6.0 (1H, m, H-3'); 6.3 (1H, br s, NH); 7.1-7.2 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 19.5 (CH_3); 32.5 ($C_{(4')}$); 33.6 ($C_{(5')}$); 41.5 (SCH_3); 46.1 ($C_{(1')}$); 126.1 ($C_{(6)}$); 128.5 ($C_{(3')}$); 131.6 ($C_{(5)}$); 132.1 ($C_{(2)}$); 134.1 ($C_{(2')}$); 137.2 ($C_{(4)}$); 146.0 ($C_{(1)}$). Found, %: C 61.90; H 6.65; N 5.34; S 12.54. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.82; N 5.57; S 12.76.

N-Toluenesulfonyl-2-(cyclopent-2-en-1-yl)-6-methylaniline (4c). A mixture of 2-(cyclopent-2-en-1-yl)-6-methylaniline (6 mmol), *p*-toluenesulfonyl chloride (9 mmol), and pyridine (10 ml) was maintained at room temperature for 24 h. Water (2 ml) was added, and the pyridine was evaporated in vacuum. The residue was dissolved in $CHCl_3$ (40 ml), washed with 10% $NaHCO_3$ solution (20 ml), with water (20 ml), and dried over Na_2SO_4. The solvent was evaporated in vacuum, and the residue recrystallized from ethanol. Yield 98.4%; mp 132-135°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.0 (6H, m, $3CH_2$); 2.1 (3H, s, CH_3); 4.1 (1H, m, CH); 5.4 (2H, m, 2CH); 6.2 (1H, s, NH); 7.0 (2H, d, *J* = 8.1, H-3",5"); 7.1 (1H, t, J = 7.0, H-4); 7.3 (2H, m, H-3,5); 7.6 (2H, d, *J* = 8.1, H-2",6"). Found, %: C 69.67; H 6.43; N 4.27; S 9.77. $C_{19}H_{20}NO_2S$. Calculated, %: C 69.69; H 6.46; N 4.28; S 9.79.

N-Methanesulfonyl-3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5a). A solution of compound **4a** (5 mmol) and I_2 (10 mmol) in CH_2Cl_2 (25 ml) was maintained at 20°C, checking the progress of the reaction by TLC. At the disappearance of the initial sulfonanilamide **4a** the reaction mixture was diluted with CH_2Cl_2 (50 ml), and the solid was filtered off. The organic solution was washed with 10% $Na_2S_2O_3$ solution (60 ml), with water (2 × 20 ml), and dried over Na_2SO_4. After removing the solvent in vacuum, the residue was recrystallized from ethanol. Yield 96.8%; mp 150-153°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.8, (1H, dddd, $J_{H\text{-}2b,H\text{-}3}$ = 4.6, $J_{H\text{-}2b,H\text{-}1b}$ = 6.5, $J_{H\text{-}2b,H\text{-}1a}$ = 12.6, J_{gem} = 14.1, H-2b); 1.9 (1H, dd, $J_{H\text{-}1b,H\text{-}2b}$ = 6.5, J_{Hgem} = 12.6, H-1b); 2.0 (1H, dd, $J_{H\text{-}2a,H\text{-}1a}$ = 6.0, J_{gem} = 14.1, H-2a); 2.7 (1H, tdd, $J_{H\text{-}1a,H\text{-}2a}$ = 6.0, $J_{H\text{-}1a,H\text{-}2b}$ = 12.6, $J_{H\text{-}1a,H\text{-}8b}$ = 8.6, J_{gem} = 12-6, H-1a); 2.9 (3H, s, CH_3); 4.0 (1H, t, $J_{H\text{-}8b,H\text{-}3a}$ = 8.6, $J_{H\text{-}8b,H\text{-}1a}$ = 8.6, H-8b); 4.8 (1H, d, $J_{H\text{-}3,H\text{-}2b}$ = 4.6, H-3); 4.9 (1H, d, $J_{H\text{-}3a,H\text{-}8b}$ = 8.6, H-3a); 7.1 (1H, t, *J* = 7.5, H Ar); 7.1-7.2 (2H, m, H Ar); 7.4 (1H, d, *J* = 7.6, H Ar). Found, %: C 39.01; H 2.90; I 34.21; N 3.33; S 8.40. $C_{12}H_{14}INO_2S$. Calculated, %: C 39.68; H 3.88; I 34.94; N 3.86; S 8.83.

N-Methanesulfonyl-3-iodo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5b). Compound **4b** (2 mmol) and I_2 (4 mmol) were dissolved in CH_2Cl_2 (10 ml). The mixture was processed analogously to compound **5a**. Yield 37%; mp 85-97°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.5-2.2 (4H, m, $2CH_2$); 2.4 (3H, s, CH_3); 3.0 (3H, s, CH_3); 3.9 (1H, dt, *J* = 3.0, *J* = 8.1, H-8b); 4.00 (1H, dt, *J* = 6.1, *J* = 7.9, H-3); 5.0 (1H, dd, *J* = 6.1, *J* = 8.1, H-3a); 7.0-7.2 (3H, m, H Ar). Found, %: C 41.06; H 3.89; I 33.22; N 3.29; S 8.16. $C_{13}H_{16}INO_2S$. Calculated, %: C 41.39; H 4.27; I 33.64; N 3.71; S 8.50.

N-Toluenesulfonyl-3-iodo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5c). Compound **4c** (1.2 mmol) and I_2 (2.4 mmol) were dissolved in CH_2Cl_2 (10 ml). The mixture was processed analogously to compound **5a**. Yield 65%; mp 174-177°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.5-1.8 (2H, m, CH_2); 1.9-2.0 (2H, m, CH_2); 2.1-2.2 (2H, m, CH_2); 2.4 (3H, s, CH_3); 2.6 (3H, s, CH_3); 2.8 (1H, dt, *J* = 3.0, *J* = 7.4, H-8b); 4.1 (1H, dt, *J* = 5.0, *J* = 6.0, H-3); 4.7 (1H, dd, *J* = 5.0, *J* = 7.7, H-3a); 6.8 (1H, d, *J* = 6.0, H-8); 7.0-7.2 (4H, m, H Ar); 7.3 (2H, d, *J* = 8.3, H-2',5'). Found, %: C 49.90; H 4.05; I 27.68; N 2.74; S 6.68. $C_{19}H_{20}INO_2S$. Calculated, %: C 50.34; H 4.45; I 27.99; N 3.09; S 7.07.

N-Methanesulfonyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (6a). A solution of compound **5a** (1.4 mmol) in DMF (2 ml) was heated at 180-200°C for 15 h. The solvent was evaporated in vacuum, the residue dissolved in CH_2Cl_2 (50 ml), and washed with water (2 × 20 ml). The organic phase was dried over Na_2SO_4, the solvent removed in vacuum, and the residue recrystallized from EtOH. Yield 90%; mp 115-118°C (EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.5 (1H, dq, J_1 = 1.9, J_{gem} = 16.9, H-1a); 2.8 (3H, s, CH_3); 2.9 (1H,

qdd, J_1 = 2.0, J_2 = 8.5, J_{gem} = 16.9, H-1b); 4.0 (1H, t, J = 8.5, H-8b); 5.4 (1H, d, J = 8.5, H-3a); 5.8 (1H, dd, J = 2.0, J = 6.2, H-2); 5.9 (1H, dd, J = 1.9, J = 6.2, H-3); 7.0 (1H, t, J = 7.5, H-6); 7.1-7.2 (2H, m, H-7,8); 7.32 (1H, d, J = 7.4, H-5). ^{13}C NMR spectrum, δ, ppm: 35.7 (CH_3); 39.6 ($C_{(1)}$); 42.2 ($C_{(8b)}$); 73.2 ($C_{(3a)}$); 114.9 ($C_{(7)}$); 124.1 ($C_{(5)}$); 125.0 ($C_{(6)}$); 128.1 ($C_{(8)}$); 129.4 ($C_{(2)}$); 133.7 ($C_{(3)}$); 135.8, 140.0 ($C_{(4a)}$, $C_{(8a)}$). Found, %: C 60.91; H 2.17; N 5.21; S 13.32. $C_{12}H_{13}NO_2S$. Calculated, %: C 61.25; H 5.57; N 5.95; S 13.63.

N-Methanesulfonyl-5-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (6b). A solution of compound **5b** (0.4 mmol) in piperidine (10 ml) was heated at 110°C for 4 h. The solvent was evaporated in vacuum, the residue dissolved in CH_2Cl_2 (50 ml), and washed with water (2 × 20 ml). The organic phase was dried over Na_2SO_4, and after removing the solvent in vacuum the yield of crude **6b** was 99%. According to the spectral characteristics this was the sole product. After recrystallization from EtOH the yield of amide **6b** was 82.8%; mp 156-159°C (EtOH). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.3 (3H, s, CH_3); 2.5 (1H, d, J_{gem} = 16.7, H-1a); 2.6 (3H, s, CH_3); 2.8 (1H, ddq, J_1 = 2.0, J_2 = 7.2, J_{gem} = 16.7, H-1b); 4.0 (1H, t, J = 7.2, H-8b); 5.4 (1H, dq, J = 2.0, J = 7.2, H-3a); 5.63 (1H, dddd, J = 0.8, J = 1.4, J = 2.0, J = 6.4, H-2); 5.7 (1H, dddd, J = 0.7, J = 0.9, J = 2.0, J = 6.4, H-3); 7.0-7.1 (3H, m, H Ar). Found, %: C 62.28; H 5.79; N 5.24; S 12.41. $C_{13}H_{15}NO_2S$. Calculated, %: C 62.63; H 6.06; N 5.62; S 12.86.

N-Toluenesulfonyl-5-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (6c). A solution of compound **5c** (1.2 mmol) in piperidine (2 ml) was heated at 110°C for 4 h. The solvent was evaporated in vacuum, the residue was dissolved in CH_2Cl_2 (50 ml), and washed with water (2 × 20 ml). The organic phase was dried over Na_2SO_4, and after removing the solvent in vacuum the yield of crude **6c** was 96%. After recrystallization from EtOH yield 60%; mp 165-168°C (EtOH). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.3 (1H, d, J_{gem} = 16.6, H-1a); 2.4 (3H, s, CH_3); 2.6 (3H, s, CH_3); 2.6 (1H, ddd, J_1 = 2.0, J_2 = 7.6, J_{gem} = 16.6, H-1b); 2.8 (1H, t, J = 7.0, H-8b); 5.2 (1H, dq, J = 2.0, J = 7.0, H-3a); 5.7 (1H, dd, J = 2.0, J = 6.0, H-2); 5.8 (1H, dd, J = 1.9, J = 6.0, H-3); 6.8 (1H, d, J = 7.0, H Ar); 7.0-7.1 (4H, m, H Ar); 7.3 (2H, d, J = 8.6, H-2',5'). Found, %: C 69.76; H 5.47; N 3.98; S 9.57. $C_{12}H_{13}NO_2S$. Calculated, %: C 70.13; H 5.88; N 4.30; S 9.85.

3-(5-Methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indolyl)pyridinium Iodide (8). A solution of amine **7** (3 mmol) in MeCN (20 ml) and pyridine (6 mmol) was heated at 75-80°C for 6-8 h. The solvent was evaporated in vacuum, the residue dissolved in hot water, and decanted from the oily insoluble solid. The crystals of compound **8**, which precipitated on cooling to room temperature, were filtered off, and dried in vacuum. Yield 57%; mp 203-205°C (H_2O). IR spectrum, ν, cm^{-1}: 3220 (NH). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.6-1.8 (2H, m, CH_2); 2.2-2.4 (2H, m, CH_2); 4.1 (1H, m, H-8b); 4.6 (1H, dd, J = 1.0, J = 7.0, H-3a); 4.9 (1H, m, H-3); 6.0 (1H, br s, NH); 6.6 (1H, t, J = 7.3, H-7); 6.8 (1H, d, J = 7.3, H Ar); 6.9 (1H, d, J = 7.3, H Ar); 8.2 (2H, m, H-3',5'); 8.7 (1H, t, J = 7.7, H-4'); 9.3 (2H, d, J = 5.8, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 16.8 (CH_3); 31.1, 32.5 ($2CH_2$); 46.0 ($C_{(8b)}$); 69.1 ($C_{(3)}$); 79.7 ($C_{(3a)}$); 117.9 ($C_{(8a)}$); 118.0 ($C_{(7)}$); 128.2 ($C_{(3',5')}$); 128.4 ($C_{(8)}$); 130.8 ($C_{(5)}$); 143.6 ($C_{(2',6')}$); 145.6 ($C_{(4')}$); 148.3 ($C_{(4a)}$). Found, %: C 53.68; H 5.36; I 33.25; N 7.11. $C_{17}H_{19}IN_2$. Calculated, %: C 53.98; H 5.06; I 33.55; N 7.41.

3-Iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5d). Compound **4d** (3 mmol) and I_2 (6 mmol) were dissolved in CH_2Cl_2 (10 ml). Processing was analogous to compound **5a**. Yield 82%. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.8-2.7 (4H, m, $2CH_2$); 3.8 (1H, br s, NH); 4.0 (1H, t, J = 8.0, H-8b); 4.2 (1H, m, H-3); 4.8 (1H, dd, J_1 = 1.1, J_2 = 8.0, H-3a); 6.5 (1H, d, J = 7.8, H Ar); 6.7 (1H, dt, J_1 = 0.9, J_2 = 8.3, H Ar); 7.0-7.1 (2H, m, H Ar). Found, %: C 46.32; H 4.23; I 44.49; N 4.90. $C_{11}H_{12}IN$. Calculated, %: C 46.34; H 4.24; I 44.51; N 4.91.

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