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REACTION OF THE N-MESYLATES OF 1,3a,4,8b-TETRAHYDROCYCLOPENTA[*b*]INDOLES AND 3,4,4a,9a-TETRAHYDROCARBAZOLES WITH DIMETHYLDIOXIRANE AND BROMINE

R. R. Gataullin[2] R. R. Ishberdina[3], A. V. Antipin[2], K. Yu. Suponitskii[1], N. N. Kabal'nova[2], O. V. Shitikova[2], L. V. Spirikhin[2], M. Yu. Antipin[1], and I. B. Abdrakhmanov[2]

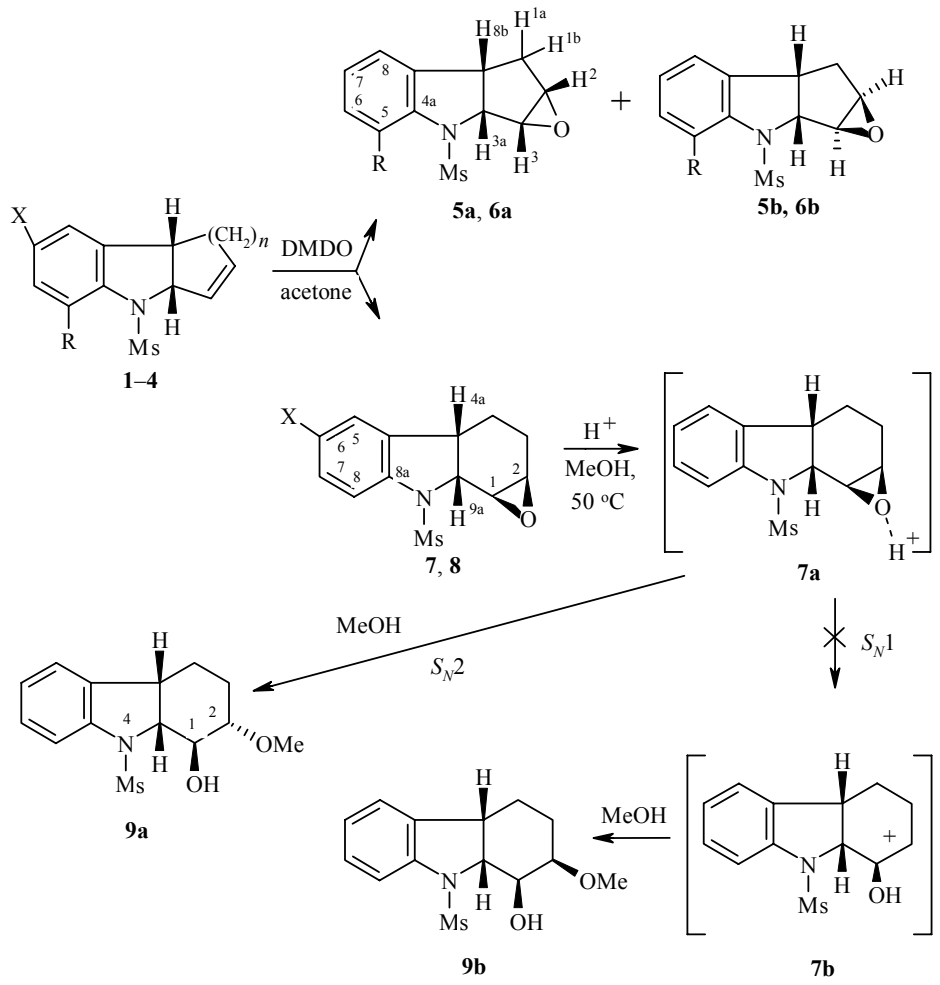
In reaction with dimethyldioxirane N-mesyl-1,3a,4,8b-tetrahydrocyclopenta[b]indoles and N-mesyl-3,3,4a,9a-tetrahydrocarbazoles mostly form the trans-epoxide. The reaction with molecular bromine leads to the product from halogenation in the aromatic ring, i.e., the corresponding N-mesyl-7-bromo-1,3a,4,8b-tetrahydrocyclopenta[b]indole or N-mesyl-6-bromo-3,4,4a,9a-tetrahydrocarbazole.

Keywords: dimethyldioxirane, tetrahydrocarbazoles, tetrahydrocyclopenta[*b*]indoles, X-ray crystallographic analysis.

Cycloalka[*b*]indolines are present in a significant number of natural compounds and medicinal preparations and find use in the synthesis of alkaloid-like systems. For this reason the development of new methods for their production has attracted the attention of a wide range of researchers [1-3]. Indolines with an unsaturated double bond in the alicyclic fragment of the molecule are also of interest as intermediates in the synthesis of a series of alkaloids. Earlier we proposed a method for the production of such compounds from the corresponding products from the halocyclization of *ortho*-(2-cycloalken-1-yl)anilines. In the present work we investigated the reactions of indolines **1-3** synthesized in this way with electrophilic reagents [4].

It was established that the reaction of compounds **1-4** with dimethyldioxirane (DMDO) leads to the epoxides **5a**,**b**, **6a**,**b**, **7**, and **8**. In the case of the oxidation of compounds **1** and **2** the epoxides **5a**,**b** and **6a**,**b** were obtained, and the ratio of the **a** and **b** isomers amounted to approximately 1:19. During the oxidation of the carbazoles **3** and **4** only the respective epoxides **7** and **8** were obtained. Treatment of the epoxide **7** with the cation exchanger KU-2-08 in methanol led to the single hexahydrocarbazole **9a** with a good yield. Since only one product was obtained, we supposed that the reaction took place by the S_N2-substitution mechanism at the stage of the formation of the protonated epoxide **7a**. In the case where the carbocation **7b** was formed in the reaction mixture the isomer **9b** could also be produced in the reaction as a result of subsequent attack on the carbocation **7b** by the methoxyl particle (methanol) from two sides of the plane.

[1] N. A. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813. [2] Institute of Organic Chemistry, Ufa Science Center of the Russian Academy of Sciences, Ufa 450054; e-mail: chemorg@anrb.ru, railg@rambler.ru. [3] Bashkir State Agrarian University, Department of General Chemistry, Ufa 450003, Russia.. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1306-1313, September, 2006. Original article submitted March 30, 2005.



5a, **6a** **5b, 6b** **1–4** **7**, **8** **7a** **9a** **9b** **7b**

1 R = X = H, *n* = 1; **2** R = Me, X = H, *n* = 1; **3** R = X = H, *n* = 2;
4 R = H, X = Br, *n* = 2; **5** R = H; **6** R = Me; **7** X = H; **8** X = Br

The orientation of the functional groups in the epoxides was established by spectral methods, and the structure of compound **5b** was also confirmed by X-ray crystallographic analysis. A general view of the molecule is shown in Fig. 1.

The two five-membered rings are quite flat. The mean-square deviations amount to 0.062 Å for $C_{(4)}$–$N_{(1)}$–$C_{(5)}$–$C_{(10)}$–$C_{(11)}$ and 0.066 Å for $C_{(1)}$–$C_{(2)}$–$C_{(3)}$–$C_{(4)}$–$C_{(11)}$. The former lies in the plane of the benzene ring, while the bending angle between the five-membered rings is 60.3(1)°. The angle between the three-membered and corresponding five-membered rings amounts to 79.6(1)°. The $C_{(4)}$–$N_{(1)}$ and $C_{(3)}$–$O_{(1)}$ bonds have the *trans* configuration [the $N_{(1)}$–$C_{(4)}$–$C_{(3)}$–$O_{(1)}$ torsion angle is 170.6(2)°] or the *anti* configuration of the epoxy- and nitrogen-containing rings. (The designations of C, O, and N correspond to Fig. 1.) The $H_{(3)}$–$C_{(3)}$–$C_{(4)}$–$H_{(4)}$ torsion angle is 72.3(1.7) Å, i.e., is close to 90°, while the spin–spin coupling constant between the respective protons is close to zero. The protons at the bridgehead atoms $C_{(4)}$ and $C_{(11)}$ have a mutual *cis* configuration [the $H_{(4)}$–$C_{(4)}$–$C_{(11)}$–$H_{(11)}$ angle is 13(2)°], as confirmed by the spin–spin coupling constant J = 8.6 Hz. The $H_{(1a)}$ and $H_{(1b)}$ protons are in the skew conformation in relation to $H_{(11)}$ [the $H_{(11)}$–$C_{(11)}$–$C_{(1)}$–$H_{(1a)}$ and $H_{(11)}$–$C_{(11)}$–$C_{(1)}$–$H_{(1b)}$ angles are equal to -22(2) and -129(2)° respectively], and their spin–spin coupling constants are 6.0-8.8 Hz. The $H_{(2)}$ and $H_{(3)}$ protons are directed along the ring and do not have large spin–spin coupling constants $J_{2\text{-}3} = J_{2\text{-}1a}$ = 2.0 Hz.

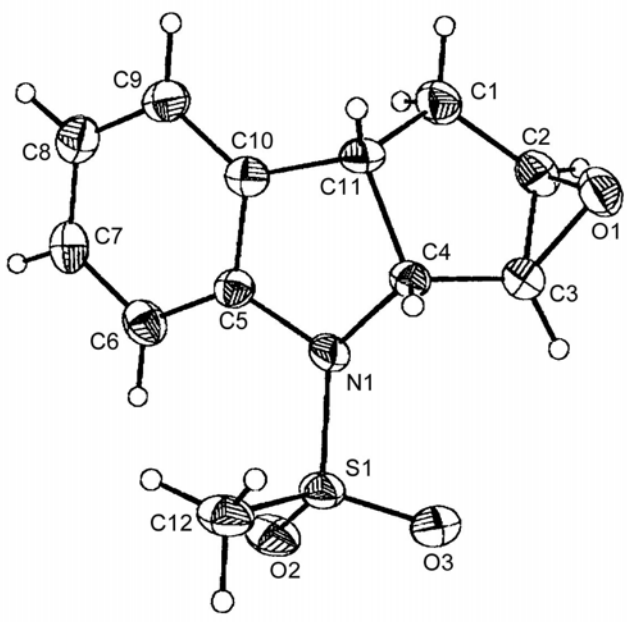


Fig. 1. A general view of the molecule of **5b** and the thermal ellipsoids (50%).

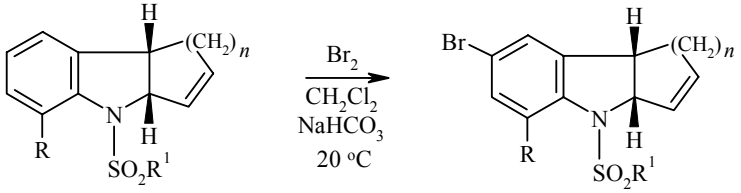
The spectral data for the minor isomer **5a** were obtained from the spectrum of the mixture of isomers **5a**-**5b** (95:5). The ^{13}C chemical shifts of the *syn*-**5a** and *anti*-**5b** isomers are close ($\Delta\delta_{max}$ = 1.5 ppm), due to the possibility of conformational mobility in the protecting group at the nitrogen, on account of which the conformation of the cyclopentane ring changes. In the ^{1}H NMR spectrum the signals of the diastereotopic protons of the AB system at $C_{(1)}$ differ most. In the *syn* isomer **5a** they resonate in the form of a complex multiplet at 2.4 ppm, whereas in the *anti* isomer **5b** the shifts of these protons differ by almost 1 ppm, due to the different 1,2-interaction of the epoxide ring in the *syn* and *anti* orientations.

The signal of H-3a in the *anti* isomer **5b** is screened by the epoxide group located in the *syn* position in relation to it. Its signal is therefore in the upfield region ($\Delta\delta$ = 0.2 ppm) compared with the *syn* isomer.

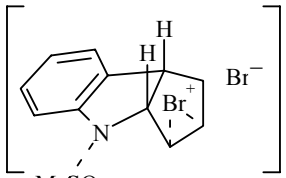
The analogous isomers **6a**,**b**, containing an *ortho*-methyl group in the aromatic ring, were obtained and were characterized by spectral methods. The main isomer **6b** was characterized in the individual form, and it was assigned the *anti* structure. The presence of the minor isomer **6a** was detected in the spectrum of the mixture of isomers **6b**-**6a** (93:7). The minor isomer **6a** was characterized from an enriched mixture **6a**-**6b** (1:1). In these compounds the mobility of the mesyl group is restricted by the presence of the *ortho* substituent in the aromatic part. The mesyl substituent is deflected from the plane of the ring in the *anti* direction in relation to the cyclopentane fragment. As a result the screening of the carbon atoms of the cyclopentane ring is reduced as demonstrated in the ^{13}C NMR spectra, and they are 5-2 ppm downfield in **6b** compared with **5b**. Here the size of the dihedral angles between the $H_{(2)}$, $H_{(3)}$, $H_{(3a)}$, and $H_{(8b)}$ protons in the cyclopentane ring remains unchanged, and the angles between $H_{(8b)}$ and $H_{(1a)}$, $H_{(1b)}$ change, as shown by the value of $J_{8b\text{-}1a}$ = 2.3 Hz (instead of 6.0 Hz).

The chemical shifts and the spin–spin coupling constants in the ^{1}H NMR spectrum of compound **9** were assigned unambiguously by the double resonance method. Compound **9** is the product from *trans* opening of the epoxide with the diaxial arrangement of the hydroxyl and methoxyl groups since each of the protons $H_{(1)}$ and $H_{(2)}$ has two diaxial spin–spin coupling constants $J_{1,4}$ = 8.3, $J_{(1,2)}$ = 9.5, and $J_{2,3a}$ = 11.0 Hz [5]. The arrangement of the hydroxyl groups and the configuration of this center are determined from the chemical shift of the $H_{(1)}$ proton and its spin–spin coupling constant [5].

As distinct from epoxidation, the reaction of compounds **1-3** and **10** with Br_2 leads to the product from electrophilic substitution in the aromatic ring **4** and **11-13**. The formation of these bromides is unexpected since in terms of the accumulated theories the olefinic CHC bond has greater reactivity than the aromatic ring in reactions with bromine. In this case one of the probable reasons is the following. The double bond of the cycloalkene fragment participates in the reaction normally with the formation of the bromonium complex **A**.



1–3, **10** **4**, **11–13**



A

1-4 R^1 = Me; **10** R = H, R^1 = *p*-C_6H_4Me, *n* = 2; **11** R = H, R^1 = Me, *n* = 1; **12** R = R^1 = Me, *n* = 1; **13** R = H, R^1 = *p*-C_6H_4Me, *n* = 2

However, *trans* attack on this complex by the Br^- anion probably does not occur on account, probably, of steric hindrances, and it is destroyed. Since electrophilic addition, which has a higher rate than electrophilic substitution in the aromatic ring, does not occur, it is the latter path that is realized.

The composition and structure of the obtained halogen derivatives were established by spectral methods and were confirmed by elemental analysis. In the aliphatic region the spectra of compounds **4** and **11-13** were similar to the spectra of the initial heterocycles, whereas in the aromatic region substantial changes were observed in the chemical shifts and the multiplicities of the signals for the protons and the carbon atoms.

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 deuterochloroform with TMS as internal standard.

Silufol plates from Lyuminofor (Russia) were used for qualitative analysis by TLC with detection by UV light (λ 254 nm) and iodine. The mass spectra were obtained on an MX 1320 (70 eV) spectrometer. The melting points were determined on a Boetius bench.

X-ray Crystallographic Investigation. The crystals for X-ray crystallographic analysis were grown from methanol (50 g of the substance **5b** in 2 ml of methanol); at 120 K, monoclinic, space group $P2_1/n$; a = 5.2089(14), b = 8.988(2), c = 24.371(6) Å; β = 90.092(5)°; V = 1141.0(5) $Å^3$; Z = 4; d_{calc} = 1.463 g/cm^3; μ = 0.279 mm^{-1}. The intensities of 5850 reflections were measured on a SMART 1000 CCD diffractometer (λMoKα = 0.71073, graphite monochromator, 2θ < 56°) at 120 K. The initial set of measured intensities was processed by SAINT Plus [6] and SADABS [7] software. The structure was interpreted by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation for the non-hydrogen atoms in F^2_{hkl}. The hydrogen atoms were located from an electron density synthesis and were refined in isotropic

approximation. During refinement 2752 unique reflections were used (R_{int} = 0.0366). The convergence of the refinement in all the unique reflections wR_2 = 0.1420, GOF 0.998 [R_1 = 0.0571 in 1796 reflections with $I > 2\sigma(I)$]. All the calculations were performed on an IBM PC AT using SHELXTL-97 software [8]. Elemental analysis was performed on an H-N Analyzer M-185B. Column chromatography was carried out on 40/70 silica gel supplied by Lancaster.

N-Methylsulfonyl-6-bromo-4,4a,9,9a-tetrahydrocarbazole (4). To a solution of (0.2 g, 0.8 mmol) of compound **3** in methylene chloride (10 ml) while stirring we added dropwise Br_2 (0.128 g, 0.8 mmol) in methylene chloride (1 ml). The reaction mixture was left at 20°C for 18 h with constant stirring while the reaction was monitored by TLC. When the initial amine had disappeared the reaction mixture was diluted with methylene chloride (50 ml) and washed with a 10% solution of sodium bicarbonate (2 × 20 ml) and with water (2 × 50 ml). The organic layer was dried over sodium sulfate. The solvent was removed under vacuum. Yield 0.125 g (48%), and the product was an amorphous mass; R_f 0.6 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.93-2.13 (4H, m, $2CH_2$); 2.93 (3H, s, CH_3); 3.71 (1H, t, J_1 = 5.0, J_2 = 8.5, H-4a); 4.84 (1H, dd, J_1 = 1.5, J_2 = 8.5, H-9a); 5.88 (1H, ddd, J_1 = 1.3, J_2 = 3.0, J_3 = 10.0, H-2); 6.00 (1H, dd, J_1 = 1.5, J_2 = 10.0, H-1); 7.23 (1H, s, H-5); 7.25 (1H, d, *J* = 7.0, H-7); 7.33 (1H, d, *J* = 7.0, H-8). ^{13}C NMR spectrum, δ, ppm: 20.5 ($C_{(4)}$), 23.0 ($C_{(3)}$); 37.4 ($C_{(4a)}$); 39.0 (CH_3); 61.7 ($C_{(9a)}$); 116.7 ($C_{(6)}$); 116.8 ($C_{(8)}$); 125.0 ($C_{(1)}$); 126.9 ($C_{(7)}$); 130.9 ($C_{(5)}$); 132.1 ($C_{(2)}$); 136.7 ($C_{(4b)}$); 140.5 ($C_{(8a)}$). Found, %: C 47.55; H 4.2; Br 24.32; N 4.26; S 9.74. $C_{13}H_{14}BrNO_2S$. Calculated, %: C 47.57; H 4.3; Br 24.34; N 4.27; S 9.77.

Oxidation with Dimethyldioxirane (General Procedure). The substrate (~0.1 mmol) was placed in a reaction vessel and was dissolved in the smallest amount of acetone (~1-2 ml). A solution of dimethyldioxirane was the added in portions of ~1 ml at 5-min intervals at room temperature with constant stirring. The initial concentration of dimethyldioxirane was ~70 mmol/l. The substrate–oxidant ratio was 1:1 or 1:2, depending on the substrate. The end of the reaction was determined from the consumption of the substrate by TLC. After the reaction the solvent was evaporated, and the products were analyzed.

(2*S*,3*R*,3a*R*,8b*S*)-N-Methylsulfonyl-2,3-epoxy-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5a). The product was analyzed in a mixture with compound **5b** in a **5b**–**5a** ratio of 95:5. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (1H, dd, *J* = 7.0, J_{gem} = 14.5, H-1a); 2.44 (1H, d, J_{gem} = 14.5, H-1b); 3.08 (3H, s, CH_3); 3.90 (1H, br. s, H-3); 4.83 (1H, dd, J_{3a-3} = 2.0, J_{3a-8b} = 8.5, H-3a); 7.08 (1H, t, J_{7-6} = J_{7-8} = 7.5, H-7); 7.17 (1H, d, J_{7-8} = 7.5, H-8); 7.21 (1H, dd, J_{6-7} = 7.5, J_{6-5} = 8.1, H-6); 7.41 (1H, d, J_{5-6} = 8.1, H-5). ^{13}C NMR spectrum, δ, ppm: 33.47 ($C_{(1)}$); 37.22 (CH_3); 42.58 ($C_{(8b)}$); 55.39 ($C_{(2)}$); 60.34 ($C_{(3)}$); 68.22 ($C_{(3a)}$); 112.41 ($C_{(6)}$); 123.39 ($C_{(7)}$); 123.79 ($C_{(6)}$); 127.78 ($C_{(8)}$); 133.70 ($C_{(8a)}$); 141.26 ($C_{(4a)}$).

(2*R*,3*S*,3a*R*,8b*S*)-N-Methylsulfonyl-2,3-epoxy-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (5b). This compound was isolated by chromatography of the dry residue after removal of the solvent from the reaction mixture obtained during the oxidation of compound **1** (0.2 g, 0.8 mmol) with dimethyldioxirane. Yield of compound **5b** 0.199 g (95%); mp 145-147°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.80 (1H, ddd, J_{1a-2} = 2.0, J_{1a-8b} = 6.0, J_{gem} = 14.5, H-1a); 2.63 (1H, d, J_{1b-8b} = 8.8, J_{gem} = 14.5, H-1b); 2.90 (3H, s, CH_3); 3.60 (1H, t, J_{2-1a} = J_{2-3} = 2.0, H-2); 3.75 (1H, ddd, J_{8b-1b} = 6.0, J_{8b-1a} = 8.8, J_{8b-3a} = 8.6, H-8b); 4.09 (1H, d, J_{3-2} = 2.0, H-3); 4.60 (1H, d, J_{3a-8b} = 8.6, H-3a); 7.08 (1H, t, J_{7-6} = J_{7-8} = 7.5, H-7); 7.17 (1H, d, J_{7-8} = 7.5, H-8); 7.21 (1H, dd, J_{6-7} = 7.5, J_{6-5} = 8.1, H-6); 7.41 (1H, d, J_{5-6} = 8.1, H-5). ^{13}C NMR spectrum, δ, ppm: 33.81 ($C_{(1)}$); 36.59 (CH_3); 42.98 ($C_{(8b)}$); 59.18 ($C_{(2)}$); 60.15 ($C_{(3)}$); 68.88 ($C_{(3a)}$); 113.73 ($C_{(5)}$); 124.33 ($C_{(7)}$); 124.74 ($C_{(6)}$); 128.24 ($C_{(8)}$); 134.25 ($C_{(8a)}$); 141.26 ($C_{(4a)}$). Found %: C 58.83; H 5.69; N 5.26; S 12.05. $C_{13}H_{15}NO_3S$. Calculated, %: C 58.85; H 5.70; N 5.28; S 12.08.

(2*S*,3*R*,3a*R*,8b*S*)-N-methylsulfonyl-2,3-epoxy-3-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta-[*b*]indole (6b). This compound was isolated by chromatography of the dry residue after removal of the solvent from the reaction mixture obtained during the oxidation of compound **2** (0.1 g, 0.4 mmol) with dimethyldioxirane. Yield compound **6b** 0.098 g (93%), and the product was an amorphous substance; R_f 0.4 (C_6H_6–EtOAc, 0.8:0.2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 (1H, td, J_{1a-8b} = J_{1a-2} = 2.3, J_{gem} = 14.7, H-1a); 2.50 (3H, s, Ar CH_3); 2.51 (1H, dd, J_{1b-8b} = 7.2, J_{gem} = 14.7, H-1b); 2.72 (3H, s, CH_3); 3.40 (1H, t,

$J_{2\text{-}1a} = J_{2\text{-}3} = 2.3$, H-2); 3.70 (1H, d, $J_{2\text{-}3} = 2.3$, H-3); 3.95 (1H, dt, $J_{8b\text{-}1a} = 2.3$, $J_{8b\text{-}3a} = J_{8b\text{-}1b} = 7.2$, H-8b); 4.70 (1H, d, $J = 7.2$, H-3a); 7.08 (1H, t, $J_{7\text{-}6} = J_{7\text{-}8} = 7.5$, H-7); 7.12 (1H, d, $J_{6\text{-}7} = 7.5$, H-6); 7.17 (1H, d, $J_{8\text{-}7} = 7.5$, H-8). ^{13}C NMR spectrum, δ, ppm: 20.39 (CH_3); 35.65 (CH_3); 36.73 (C(1')); 47.23 ($C_{(8b)}$); 59.03 ($C_{(2)}$); 62.60 ($C_{(3)}$); 68.53 ($C_{(3a)}$); 122.29 ($C_{(6)}$); 127.29 ($C_{(7)}$); 131.14 ($C_{(5)}$); 131.40 ($C_{(8)}$); 139.23 ($C_{(8a)}$); 140.27 ($C_{(4a)}$). Found, %: C 58.83; H 5.69; N 5.23; O 18.07; S 12.07. $C_{13}H_{15}NO_3S$. Calculated, %: C 58.85; H 5.70; N 5.28; O 18.09; S 12.08.

(2*R*,3*S*,3a*R*,8b*S*)-N-Methylsulfonyl-2,3-epoxy-3-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]-indole (6a). The compound was analyzed in a mixture with compound **6b** in a **6a**–**6b** ratio of 1:1. ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.30 (1H, dd, $J_{1b\text{-}8b} = 7.8$, $J_{gem} = 14.8$, H-1b); 2.40 (1H, d, $J_{gem} = 14.8$, H-1a); 2.48 (3H, s, CH_3); 2.77 (3H, s, CH_3); 3.50 (1H, br. s, H-2); 3.80 (1H, br. s, H-3); 3.98 (1H, t, $J_{8b\text{-}3a} = J_{8b\text{-}1b} = 7.8$, H-8b); 4.93 (1H, dd, $J_{3a\text{-}3} = 1.5$, $J_{3a\text{-}8b} = 7.8$, H-3a); 7.00-7.20 (3H, m, Ar). ^{13}C NMR spectrum, δ, ppm: 20.12 (CH_3); 33.15 ($C_{(1)}$); 36.30 (CH_3); 41.63 ($C_{(8b)}$); 57.80 ($C_{(2)}$); 59.80 ($C_{(3)}$); 68.59 ($C_{(3a)}$); 120.75 ($C_{(6)}$); 126.79 ($C_{(7)}$); 130.84 ($C_{(8)}$); 131.14 ($C_{(5)}$); 139.23 ($C_{(8a)}$); 140.77 ($C_{(4a)}$).

(1*S*,2*R*,4a*S*,9a*R*)-N-Methylsulfonyl-1,2-epoxy-1,2,3,4,4a,9a-hexahydrocarbazole (7). After removal of the solvent under vacuum from the reaction mixture obtained by oxidation of compound **3** (0.249 g, 1 mmol) with dimethyldioxirane the residue was chromatographed on a column (2 × 20 cm) through a layer of silica gel (0.25 g, eluant C_6H_6) in order to remove the resinous products. Yield 0.207 g (78%). The product was a viscous mass; R_f 0.6 (C_6H_6–EtOAc, 0.8:0.2). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.60 (1H, dt, $J_1 = 4.7$, $J_2 = 14.0$, H-3*ax*); 1.85 (1H, tdd, $J_1 = 3.3$, $J_2 = 4.7$, $J_3 = 14.0$, H-4*eq*); 1.98 (1H, tdd, $J_1 = 3.3$, $J_2 = 4.2$, $J_3 = 14.0$, H-3*eq*); 2.08 (1H, tt, $J_1 = 4.2$, $J_2 = 14.0$, H-4*ax*); 3.10 (1H, t, $J = 3.3$, H-2); 3.30 (1H, d, $J = 3.3$, H-1); 3.61 (1H, ddd, $J_1 = 3.3$, $J = 4.2$, $J_2 = 9.5$, H-4a); 4.70 (1H, d, $J = 9.5$, H-9a); 2.90 (3H, s, CH_3); 7.12-7.30 (3H, m, ArH); 7.50 (1H, d, $J = 7.5$, ArH). ^{13}C NMR spectrum, δ, ppm: 16.62 ($C_{(3)}$); 21.0 ($C_{(4)}$); 36.7 ($C_{(4a)}$); 37.4 (CH_3); 51.7 ($C_{(2)}$); 53.3 ($C_{(1)}$); 59.3 ($C_{(9a)}$); 116.1 ($C_{(7)}$); 123.9 ($C_{(8)}$); 125.1 ($C_{(5)}$); 128.5 ($C_{(6)}$); 133.2 ($C_{(4b)}$); 141.5 ($C_{(8a)}$). Found, %: C 58.84; H 5.68; N 5.25; O 18.08; S 12.06. $C_{13}H_{15}NO_3S$. Calculated, %: C 58.85; H 5.70; N 5.28; O 18.09; S 12.08.

(1*S*,2*R*,4a*S*,9a*R*)-N-Methylsulfonyl-6-bromo-1,2-epoxy-1,2,3,4,4a,9a-hexahydrocarbazole (8). This compound was obtained similarly to compound **7** from the bromide **4** (0.344 g, 1 mmol). Yield 0.33 g (96%), and the product was an amorphous substance; R_f 0.6 (C_6H_6–EtOAc, 0.8:0.2). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.65 (1H, dt, $J_1 = 3.4$, $J_2 = 14.0$, H-3*ax*); 1.80 (1H, qd, $J_1 = 4.4$, $J_2 = 14.0$, H-4*eq*); 2.01 (1H, tdd, $J_1 = 3.4$, $J_2 = 4.4$, $J_3 = 14.0$, H-3*eq*); 2.08 (1H, tt, $J_1 = 4.4$, $J_2 = 14.0$, H-4*ax*); 2.90 (3H, s, CH_3); 3.14 (1H, t, $J = 3.4$, H-2); 3.30 (1H, d, $J = 3.4$, H-1); 3.60 (1H, ddd, $J_1 = 3.4$, $J_2 = 4.4$, $J_3 = 9.5$, H-4a); 4.70 (1H, d, $J = 9.5$, H-9a); 7.23 (1H, d, $J = 1.0$, ArH); 7.40 (2H, d, $J = 1.0$, ArH). Found, %: C 45.35; H 4.08; Br 23.18; N 4.05; O 13.93; S 9.30. $C_{13}H_{14}BrNO_3S$. Calculated, %: C 45.36; H 4.10; Br 23.21; N 4.07; O 13.94; S 9.31.

N-Methylsulfonyl-2-methoxy-l,2,3,4,4a,9a-hexahydrocarbazol-1-ol (9a). A reaction mixture consisting of the epoxide **7** (0.06 g, 2 mmol) and the cation-exchanger KU-2-08 in methanol (5 ml) was left at 50°C for 1 h with constant stirring while the reaction was monitored by TLC. When the initial compound had disappeared the reaction mixture was cooled to room temperature, and the cation-exchanger was filtered off. After removal of the solvent under vacuum the yield of compound **9a** was 0.065 g (97%). The product was an amorphous mass; R_f 0.5 (C_6H_6-EtOAc, 8.5:1.5). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.19 (1H, ddt, $J_1 = 3.8$, $J_2 = 11.0$, $J_{gem} = 13.5$, H-3*ax*); 1.30 (1H, s, OH); 1.85 (1H, ddt, $J_1 = 3.8$, $J_2 = 6.0$, $J_3 = 13.5$, H-4*ax*); 2.00 (1H, qd, $J_1 = 3.8$, $J_2 = 13.5$, H-3*eq*); 2.37 (1H, dqd, $J_1 = 2.0$, $J_2 = 3.8$, $J_3 = 13.5$, H-4*eq*); 3.08 (1H, ddd, $J_1 = 3.8$, $J_2 = 9.5$, $J_3 = 11.0$, H-2*ax*); 3.19 (3H, s, OCH_3); 3.38 (1H, dd, $J_1 = 8.1$, $J_2 = 9.5$, H-1*ax*); 3.72 (1H, ddd, $J_1 = 2.0$, $J_2 = 6.0$, $J_3 = 8.1$, H-4a); 4.34 (1H, t, 7 = 8.1, H-9a); 7.05-7.16 (2H, m, ArH); 7.23 (1H, t, $J = 7.8$, ArH); 7.35 (1H, d, $J = 7.8$, ArH). ^{13}C NMR spectrum, δ, ppm: 21.4 ($C_{(4)}$); 23.7 ($C_{(3)}$); 39.7 (CH_3), 41.3 ($C_{(4a)}$); 56.9 (OCH_3); 69.7 ($C_{(9a)}$); 76.0 ($C_{(1)}$); 81.34 ($C_{(2)}$); 116.7 ($C_{(8)}$); 122.6 ($C_{(6)}$); 124.3 ($C_{(7)}$); 128.2 ($C_{(5)}$); 134.2 ($C_{(4b)}$), 141.3 ($C_{(8a)}$). Found, %: C 56.52; H 6.43; N 4.89; S 10.75. $C_{14}H_{19}NO_4S$. Calculated, %: C 56.55; H 6.44; N 4.71; S 10.78.

N-Methylsulfonyl-7-bromo-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (11). The compound was obtained similarly to compound **4** from compound **1** (0.244 g, 0.1 mmol) and Br_2 (0.166 g, 1 mmol). After removal of the solvent under vacuum the product was recrystallized from ethanol (1 ml). Yield 0.322 g (98.7%); mp 152-153°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (1H, d, *J* = 17.1, R-1*eq*); 3.07 (1H, dd, *J* = 17.1, J_1 = 9.1, H-1*ax*); 2.89 (3H, s, CH_3); 4.09 (1H, t, *J* = 8.5, H-8b); 5.38 (1H, d, *J* = 8.5, H-3a); 5.89-5.98 (2H, m, H-2,3); 7.23 (1H, d, *J* = 7.5, H-5); 7.30 (1H, s, H-8); 7.33 (1H, d, *J* = 7.5, H-6). ^{13}C NMR spectrum, δ, ppm: 37.1 (CH_3); 39.9 (CH_2); 42.2 ($C_{(8b)}$); 73.7 ($C_{(3a)}$); 116.1 ($C_{(5)}$); 116.7 ($C_{(7)}$); 128.3 ($C_{(6)}$); 128.5 ($C_{(3)}$); 131.3 ($C_{(8)}$); 133.9 ($C_{(2)}$); 138.3 ($C_{(8a)}$); 139.5 ($C_{(4a)}$). Found, %: C 45.86; H 3.83; Br 25.41; N 4.45; S 10.18. $C_{12}H_{12}BrNO_2S$. Calculated, %: C 45.87; H 3.85; Br 25.43; N 4.46; S 10.20.

N-Methylsulfonyl-7-bromo-5-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (12). The compound was obtained similarly to compound **4** from compound **2** (0.1 g, 0.4 mmol) and bromine (0.064 g, 0.4 mmol). After removal of the solvent under vacuum the product was recrystallized from ethanol (1 ml). Yield 0.129 g (98%), and the product was an amorphous mass; R_f 0.7 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3); 2.94 (3H, s, CH_3); 2.95-3.19 (2H, m, CH_2); 4.00 (1H, td, J_1 = 2.0, J_2 = 8.5, H-8b); 5.31 (1H, dd, J_1 = 1.5, J_2 = 8.5, H-3a); 5.83-5.95 (2H, m, H-2,3); 7.25 (1H, s, H-8); 7.32 (1H, s, H-6). ^{13}C NMR spectrum, δ, ppm: 19.9 (CH_3); 35.7 (CH_3); 39.1 (CH_2); 42.9 ($C_{(8b)}$); 74.4 ($C_{(3a)}$); 119.9 ($C_{(7)}$); 122.1 ($C_{(3)}$); 126.9 ($C_{(2)}$); 130.9 ($C_{(8)}$); 132.4 ($C_{(5)}$); 132.6 ($C_{(6)}$); 134.4 ($C_{(8a)}$); 140.5 ($C_{(4a)}$). Found, %: C 47.55; H 4.27; Br 24.33; N 4.25; S 9.75. $C_{13}H_{14}BrNO_2S$. Calculated, %: C 47.57; H 4.30; Br 24.34; N 4.27; S 9.77.

N-Tosyl-6-bromo-4,4a,9,9a-tetrahydrocarbazole (13). The compound was obtained similarly to compound **4** by the reaction of compound **10** (0.675 g, 2 mmol) with bromine (0.32 g, 2 mmol). After recrystallization from ethanol the yield was 0.62 g (77.5%); mp 110-113°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.81-1.95 (4H, m, $2CH_2$); 2.38 (3H, s, H-3); 3.06 (1H, m, H-4a); 4.70 (1H, dd, J_1 = 1.7, J_2 = 8.0, H-9a); 5.95 (2H, m, H-1,2); 7.12 (1H, s, H-5); 7.20 (2H, d, *J* = 8.0, H-3,5); 7.33 (1H, d, *J* = 8.4, H-7); 7.53 (1H, d, *J* = 8.4, H-8); 7.59 (2H, d, *J* = 8.5, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 19.9 ($C_{(4)}$); 21.4 (CH_3); 22.4 ($C_{(3)}$); 36.56 ($C_{(4a)}$); 61.54 ($C_{(9a)}$); 117.50 ($C_{(6)}$); 119.23 ($C_{(8)}$); 125.72 ($C_{(1)}$); 126.59 ($C_{(7)}$); 126.77 ($C_{(3',5')}$); 129.66 ($C_{(2',6')}$); 130.69 ($C_{(5)}$); 135.26 ($C_{(4')}$), 131.30 ($C_{(2)}$); 137.45 ($C_{(4b)}$); 140.84 ($C_{(8a)}$); 143.98 ($C_{(1)}$). Found, %: C 56.42; H 4.47; Br 19.75; N 3.43; S 7.91. $C_{19}H_{18}BrNO_2S$. Calculated, %: C 56.44; H 4.49; Br 19.76; N 3.46; S 7.93.

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