ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 9, pp. 1305–1309. © Pleiades Publishing, Ltd., 2007.
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# Synthesis of Oxo Derivatives of *N*-(*p*-Tolylsulfonyl)-hexahydrocycloalka[*b*]indoles

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Received November 3, 2006

**Abstract**—Hydroxymercuration–demercuration of *N*-*p*-tolylsulfonyl-4,4a,9,9a-tetrahydro-3*H*-carbazoles and *N*-*p*-tolyl(or methyl)sulfonyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles leads to the formation of the corresponding *N*-*p*-tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-2-ols and *N*-*p*-tolyl(or methyl)sulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-2-ols. The latter are oxidized to 2-oxo derivatives with potassium dichromate. The oxidation of 2-methoxy-8-methyl-*N*-*p*-tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-1-ol under analogous conditions gives 2-methoxy-8-methyl-*N*-*p*-tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-1-one.

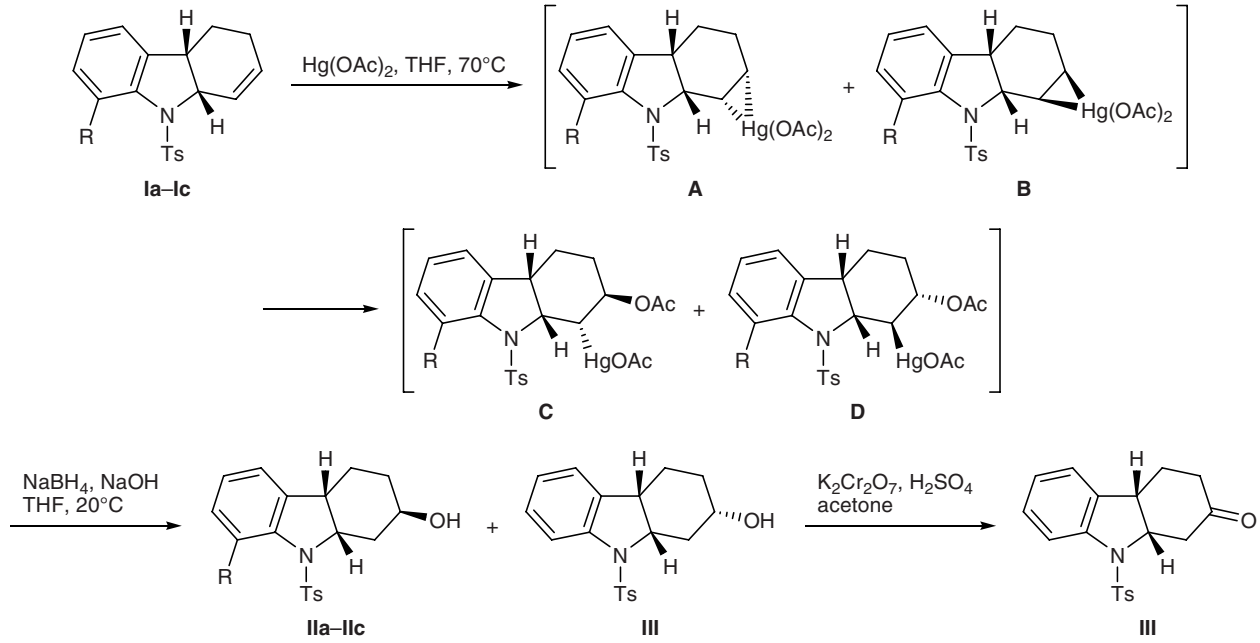
**DOI:** 10.1134/S1070428007090084

It is known that oxo derivatives of partially hydrogenated cycloalka[*b*]indoles are used in multistep syntheses of ellipticine and olivacine analogs [1–4], as well as of tetracyclic skeleton of *Aspidosperma* and *Strychnos* alkaloids [5]. In addition, some oxo derivatives were isolated from vegetable raw materials [6, 7]. Several procedures have been proposed for the synthesis of tetra- and hexahydrocycloalka[*b*]indolones [8–10]. Nevertheless, studies aimed at searching for new methods for the preparation of such compounds are in progress. In the present work we examined a scheme of synthesis of cycloalka[*b*]indol-2- and -1-ones starting from tetrahydrocycloalka[*b*]indoles which were synthesized by us previously [11].

By reaction of heterocycle **Ia** with mercury(II) acetate we obtained two alcohols **IIa** and **III** at a ratio of ~3:2 (calculated from the signal intensities in the $^1$H NMR spectrum of the product mixture). However, hydroxymercuration–demercuration of carbazoles **Ib** and **Ic** having a substituent in position *8* gave only alcohols **IIb** and **IIc**, respectively (Scheme 1). Obviously, the formation of alcohols **II** and **III** involves intermediate complexes **A** or **B** and their subsequent transformation into mercury derivatives **C** or **D**. In our case the hydroxymercuration process requires prolonged heating. The formation of both types of complexes cannot be ruled out both in the absence and in the presence of a substituent on $C^8$. It is known that mercury(II) ion has a fairly large radius. Presumably, a substituent in the *peri* position with respect to the tosyl group displaces the latter toward the cyclohexene ring, thus hindering the transformation of complex **B** into intermediate **D**. The substituent on the nitrogen atom in molecule **Ia** hampers formation of organomercury derivative **D** to a lesser extent, and the reduction of intermediates **C** and **D** with $NaBH_4$ gives two stereoisomeric alcohols **IIa** and **III**. Oxidation of alcohol mixture **IIa/III** with $K_2Cr_2O_7$ in acetone leads to ketone **IV**.

The structure of heterocyclic compounds **IIa**–**IIc**, **III**, and **IV** was determined on the basis of their analytical and spectral data. Signals in the $^1$H NMR spectra of **IIa**–**IIc** were assigned using H–H-correlation technique. The 2-H proton gives a narrow one-proton multiplet at δ 2.60–2.90 ppm; it shows no coupling with 4a-H and 9a-H. The 9a-H signal appears at δ 4.63–4.90 ppm. In the spectrum of **IIa**, the 9a-H signal is a quartet with a coupling constant *J* of 7.5 Hz (δ 4.70 ppm). The corresponding protons in compounds **IIb** and **IIc** give rise to doublets of triplets ($J_1$ = 6.5–6.7, $J_2$ = 9.93–10.9 Hz). Presumably, the hydroxy group on $C^2$ occupies axial position; therefore, the coupling constants of the equatorial 2-H proton are small ($J_{eq,ax}$ = 4–6, $J_{eq,eq}$ = 2–4 Hz) [12]. The orientation of 9a-H is close to axial, and the corresponding coupling constants are fairly large.

**Scheme 1.**




R = H (**a**), Me (**b**), MeO (**c**).

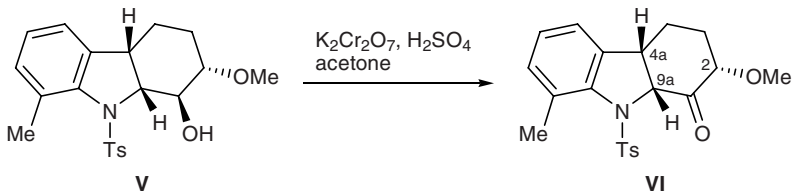
We failed to isolate compound **III** as individual substance, and its spectral parameters were determined from the $^1$H NMR spectrum of a mixture with stereoisomer **IIa** at a ratio of 2:3. The 9a-H signal of **III** is a triplet of doublets ($J_1$ = 6.4, $J_2$ = 11.0 Hz), indicating nearly axial orientation of that proton. The 2-H proton appears as a triple doublet of doublets ($J_1$ = 11.9, $J_2$ = 3.5, $J_3$ = 3.0 Hz). The large coupling constant corresponds to interaction with two axial protons, 1-H$_{ax}$ and 3-H$_{ax}$, and the small coupling constants reflect interaction with two equatorial protons, 1-H$_{eq}$ and 3-H$_{eq}$. Although the half-width of the 4a-H signal is about 20 Hz, the signal is poorly resolved.

Orientation of the hydroxy group on C$^2$ in molecules **IIa**–**IIc** was determined by NOE experiment with compound **IIa** as an example. Irradiation at a frequency corresponding to resonance of 4a-H increased the intensity of the 9a-H signal by 7.6%. Saturation of the 9a-H proton increased the intensity of the 4a-H signal by 7.0%. In both cases, no increase in the intensity of the 2-H signal was observed. Likewise, selective irradiation of the 2-H proton did not affect the intensities of the 4a-H and 9a-H signals. These data confirmed the assumed orientation of 2-H in compounds **IIa**–**IIc**.

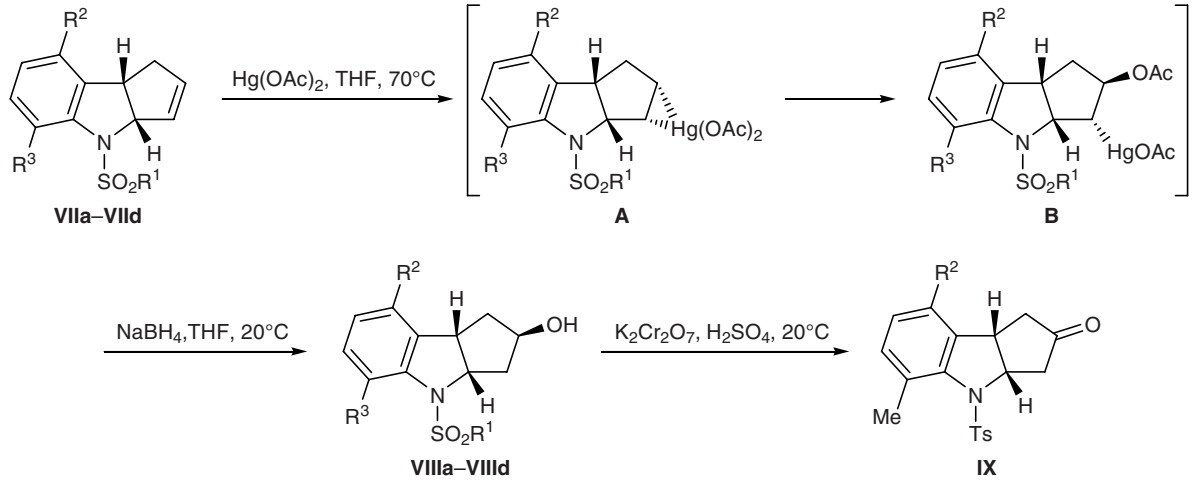
In the $^{13}$C NMR spectra (*J*-modulated spin–echo sequence) of **IIa**–**IIc**, signals from C$^1$, C$^{9a}$, and C$^{4a}$ appeared in the regions $\delta_C$ 65.2–65.4, 61.7–62.3, and 38.3–39.7 ppm, respectively. Triplet signals of the methylene carbon atoms were observed at 17.0, 26.4, and 34.0 ppm. The chemical shifts of carbon nuclei in the aromatic fragments were consistent with the calculated values.

By oxidation of compound **V** [11] with potassium dichromate under analogous conditions we obtained 1-oxo derivative **VI** in good yield (Scheme 2). Orientation of the methoxy group in molecules **V** and **VI** was refined by NOE experiment with ketone **VI**. Irradiation of the 2-H proton enhanced the 9a-H signal intensity by 2%, while irradiation of 9a-H induced increase in

**Scheme 2.**



**Scheme 3.**




$R^1$ = *p*-$MeC_6H_4$, $R^2$ = $R^3$ = H (**a**), Me (**c**); $R^2$ = H, $R^3$ = Me (**b**); $R^1$ = $R^2$ = $R^3$ = Me (**d**).

the 2-H signal intensity by 3.4%. Simultaneously, the intensity of the doublet signal from 2′-H and 6′-H in the tosyl group increased by 4%, indicating that the tosyl substituent is oriented *syn* with respect to the 9a-H proton. Irradiation of protons in the methoxy group did not affect the 9a-H and 4a-H signals, whereas saturation of the 4a-H resonance increased the 9a-H signal intensity by 4.9%. The above findings confirm the steric structure of carbazole derivatives **V** and **VI** proposed by us previously.

In the reactions of tetrahydrocyclopenta[*b*]indoles **VIIa–VIId** with mercury(II) acetate, followed by treatment with sodium tetrahydridoborate in THF we isolated alcohols **VIIIa–VIIId** as the only products. Oxidation of alcohol **VIIIb** with potassium dichromate in acetone in the presence of sulfuric acid gave ketone **IX** (Scheme 3).

Signals in the $^1$H NMR spectra of compounds **VIIIa–VIIId** were assigned using H–H-correlation technique. Orientation of the hydroxy group was determined by NOE experiments. Irradiation of the 8b-H proton increased the intensity of the 1-$H_A$ and 1-$H_B$ signals by 10.4 and 1.0%, respectively. The 2-H signal increased in intensity by 4.88% upon irradiation of 1-$H_B$, whereas the 8b-H signal intensity did not increase. On the other hand, saturation of the 1-$H_A$ resonance resulted in 5.11% gain in the 8b-H signal intensity, while the intensity of the 2-H signal increased by only 1.6%. Irradiation of 2-H gave NOEs on 1-$H_B$ (3.14%) and 2-OH (4.65%). Therefore, we presumed *trans* orientation of the 8b-H and 1-$H_B$ protons and *cis* arrangement of 1-$H_B$ and 2-H. In the $^1$H NMR spectrum of ketone **IX**, protons on $C^3$ appeared at δ 2.20 (3-$H_A$) and 2.85 ppm (3-$H_B$) as doublets of doublets with a geminal coupling constant of ~20 Hz. Signals from the 1-$H_A$ and 1-$H_B$ protons were overlapped by the methyl proton signal, and we failed to determine the corresponding coupling constant.

Thus the reactions of *N*-*p*-tolylsulfonyl derivatives of 3,4,4a,9a-tetrahydrocarbazoles and 1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles with $Hg(OAc)_2$ gave the corresponding 2-hydroxy-2,3,4,4a,9,9a-hexahydro-1*H*-carbazoles and 2-hydroxy-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles which were oxidized to 2-oxo derivatives with potassium dichromate.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument. The $^1$H and $^{13}$C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using TMS as internal reference. The elemental analyses were obtained on an M-185B CHN Analyzer. Column chromatography was performed on Lancaster LS silica gel (40–100 μm). Sorbfil plates (Sorbpolimer Ltd., Krasnodar, Russia) were used for qualitative thin-layer chromatography; spots were visualized by treatment with iodine vapor.

**Alcohols IIa–IIc, III, and VIIIa–VIIId (***general procedure***).** A solution of 2 g (6 mmol) of mercury(II) acetate in 9 ml of water was added to a solution of 0.6 mmol of compound **Ia–Ic** or **VIIa–VIId** in 15 ml of THF, and the mixture was heated for 10 h at 70–75°C. It was then cooled to room temperature, and 20 ml of a 3 M solution of sodium hydroxide and 20 ml of a 0.5 M solution of $NaBH_4$ in 3 M aqueous

sodium hydroxide were added in succession. The mercury precipitate was allowed to settle down, sodium chloride was added, the mixture was diluted with 50 ml of methylene chloride, and the organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to chromatography on a column charged with silica gel using benzene as eluent. The products were light yellow to brown oily substances.

**(2*R*,4a*S*,9a*S*)-9-*p*-Tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-2-ol (IIa).** Yield 0.16 g (77%), $R_f$ 0.51 ($C_6H_6$–EtOAc, 2:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.40–2.20 m (7H, $CH_2$, OH), 2.40 s (3H, $CH_3$), 2.90 m (1H, 4a-H), 4.12 m (1H, 2-H), 4.55 q (1H, 9a-H, $J$ = 7.5 Hz), 7.08–7.24 m (5H, $H_{arom}$), 7.60 d (2H, $H_{arom}$, $J$ = 8.2 Hz), 7.68 d (1H, $H_{arom}$, $J$ = 8.0 Hz). Found, %: C 66.23; H 6.03; N 3.86; S 9.09. $C_{19}H_{21}NO_3S$. Calculated, %: C 66.45; H 6.16; N 4.08; S 9.34.

**(2*R*,4a*S*,9a*S*)-8-Methyl-9-*p*-tolylsulfonyl-2,3,4,4a,-9,9a-hexahydro-1*H*-carbazol-2-ol (IIb).** Yield 0.17 g (79%), $R_f$ 0.63 ($C_6H_6$–EtOAc, 2:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–2.20 m (7H, $CH_2$, OH), 2.39 s (3H, $CH_3$), 2.45–2.62 m (1H, 4a-H), 2.55 s (3H, $CH_3$), 4.00 m (1H, 2-H), 4.63 d.t (1H, 9a-H, $J_1$ = 6.5, $J_2$ = 9.9 Hz), 6.83 d (1H, $H_{arom}$, $J$ = 5.0 Hz), 7.08–7.19 m (4H, $H_{arom}$), 7.47 d (2H, $H_{arom}$, $J$ = 8.2 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 17.6 ($C^4$); 19.5 and 21.3 ($CH_3$); 26.2 ($C^3$); 34.2 ($C^1$); 38.3 ($C^{4a}$); 61.7 ($C^{9a}$); 65.3 ($C^2$); 120.0, 126.3, 127.0, 129.2, 130.0 ($C^5$, $C^6$, $C^7$, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 133.1, 135.8, 138.9, 140.6, 143.5 ($C^{4b}$, $C^8$, $C^{8a}$, $C^{1'}$, $C^{4'}$). Found, %: C 67.03; H 6.38; N 3.68; S 8.71. $C_{20}H_{23}NO_3S$. Calculated, %: C 67.20; H 6.49; N 3.92; S 8.97.

**(2*R*,4a*S*,9a*S*)-8-Methoxy-9-*p*-tolylsulfonyl-2,3,-4,4a,9,9a-hexahydro-1*H*-carbazol-2-ol (IIc).** Yield 0.11 g (49%), $R_f$ 0.09 ($C_6H_6$–EtOAc, 9:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.40–2.20 m (7H, $CH_2$, OH), 2.40 s (3H, $CH_3$), 2.90 m (1H, 4a-H), 3.50 s (3H, $CH_3$), 4.05 m (1H, 2-H), 4.90 t.d (1H, 9a-H, $J_1$ = 6.7, $J_2$ = 10.9 Hz), 6.67 d (1H, $H_{arom}$, $J$ = 7.4 Hz), 6.85 d ($H_{arom}$, $J$ = 8.3 Hz), 7.10–7.20 m (3H, $H_{arom}$). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 17.8, 26.5, 34.5 ($CH_2$); 21.4 ($CH_3$); 39.7 ($C^{4a}$); 55.9 ($OCH_3$); 62.3 ($C^{9a}$); 65.4 ($C^2$); 112.2, 115.3, 127.1, 127.3, 129.1 ($C^5$, $C^6$, $C^7$, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 130.0, 137.2, 140.3, 143.2, 152.7 ($C^{4b}$, $C^8$, $C^{8a}$, $C^{1'}$, $C^{4'}$). Found, %: C 63.25; H 5.72; N 3.64; S 8.67. $C_{19}H_{21}NO_4S$. Calculated, %: C 63.49; H 5.89; N 3.90; S 8.92.

**(2*S*,4a*S*,9a*S*)-9-*p*-Tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-2-ol (III).** $R_f$ 0.21 ($C_6H_6$–EtOAc, 2:1). $^1$H NMR spectrum ($C_6D_6$), δ, ppm: 1.40–2.30 m (6H, $CH_2$), 1.77 s (3H, $CH_3$), 2.55–2.60 m (1H, 4a-H), 3.12 d.d.t (1H, 2-H, $J_1$ = 3.0, $J_2$ = 3.5, $J_3$ = 11.9 Hz), 4.35 t.d (1H, 9a-H, $J_1$ = 6.4, $J_2$ = 11.0 Hz), 6.50–7.10 m (5H, $H_{arom}$), 7.67 d (2H, $H_{arom}$, $J$ = 8.0 Hz), 7.93 d (1H, $H_{arom}$, $J$ = 7.8 Hz).

**(2*R*,3a*S*,8b*S*)-4-*p*-Tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-2-ol (VIIIa).** Yield 0.12 g (62%), $R_f$ 0.44 ($C_6H_6$–EtOAc, 2:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.60 br.s (OH), 1.80–2.35 m (4H, $CH_2$), 2.40 s (3H, $CH_3$), 3.72 d.t (1H, 8b-H, $J_1$ = 5.6, $J_2$ = 9.0 Hz), 4.35 q (1H, 2-H, $J$ = 4.5 Hz), 4.71 d.t (1H, 3a-H, $J_1$ = 7.2, $J_2$ = 9.0 Hz), 7.01–7.23 m (6H, $H_{arom}$), 7.62 d (2H, $H_{arom}$, $J$ = 8.0 Hz). Found, %: C 65.41; H 5.59; N 4.06; S 9.52. $C_{18}H_{19}NO_3S$. Calculated, %: C 65.63; H 5.81; N 4.25; S 9.73.

**(2*R*,3a*S*,8b*S*)-5-Methyl-4-*p*-tolylsulfonyl-1,2,3,-3a,4,8b-hexahydrocyclopenta[*b*]indol-2-ol (VIIIb).** Yield 0.15 g (75%), $R_f$ 0.15 ($C_6H_6$–EtOAc, 9:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.35–2.30 m (5H, $CH_2$, OH), 2.42 s (3H, $CH_3$), 2.60 s (3H, $CH_3$), 2.80 m (1H, 8b-H), 4.09 m (1H, 2-H), 4.80 q (1H, 3a-H, $J$ = 8.0 Hz), 6.80 d (1H, $H_{arom}$, $J$ = 6.0 Hz), 7.10–7.20 m (4H, $H_{arom}$), 7.30 d (2H, $H_{arom}$, $J$ = 8.2 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 19.8, 21.4 ($CH_3$); 40.6, 40.8 ($C^1$, $C^3$); 42.2 ($C^{8b}$); 67.2 ($C^{3a}$); 71.1 ($C^2$); 121.5, 127.0, 127.6, 129.1, 130.1 ($C^6$, $C^7$, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 132.7, 133.4, 139.8, 142.0, 143.7 ($C^{4a}$, $C^5$, $C^{8a}$, $C^{1'}$, $C^{4'}$). Found, %: C 66.58; H 5.92; N 3.99; S 8.95. $C_{19}H_{21}NO_3S$. Calculated, %: C 66.45; H 6.16; N 4.08; S 9.34.

**(2*R*,3a*S*,8b*S*)-5,8-Dimethyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-2-ol (VIIIc).** Yield 0.16 g (73%), $R_f$ 0.14 ($C_6H_6$–EtOAc, 9:1). $^1$H NMR spectrum, $CDCl_3$, δ, ppm: 1.50–1.75 m (4H, 3-$H_A$, $CH_2$, OH), 2.02 s (3H, $CH_3$), 2.21–2.37 m (1H, 3-$H_B$), 2.40 s (3H, $CH_3$), 2.60 s (3H, $CH_3$), 2.85 d (1H, 8b-H), 4.18 m (1H, 2-H), 4.81 q (1H, 3a-H, $J$ = 8.7 Hz), 6.90 d (1H, $H_{arom}$, $J$ = 7.6 Hz), 7.04 d (1H, $H_{arom}$, $J$ = 7.5 Hz), 7.11 d (2H, $H_{arom}$, $J$ = 4.4 Hz), 7.23 d (2H, $H_{arom}$, $J$ = 8.3 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 18.0, 19.5, 21.4 ($CH_3$); 40.2, 41.0 ($C^1$, $C^3$); 41.4 ($C^{8b}$); 66.8 ($C^{3a}$); 71.2 ($C^2$); 127.8, 128.1, 128.9, 130.1 ($C^6$, $C^7$, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 129.7, 130.9, 133.0, 139.2, 140.6, 143.6 ($C^{4a}$, $C^5$, $C^8$, $C^{8a}$, $C^{1'}$, $C^{4'}$). Found, %: C 66.95; H 6.27; N 3.68; S 8.81. $C_{20}H_{23}NO_3S$. Calculated, %: C 67.20; H 6.49; N 3.92; S 8.97.

**(2*R*,3a*S*,8b*S*)-5,8-Dimethyl-4-methylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-2-ol**

**(VIIId).** Yield 0.11 g (68%), $R_f$ 0.34 ($C_6H_6$–EtOAc, 9:1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 br.s (1H, OH), 1.65–1.85 m (3H, 3a-H, $CH_2$), 2.21 s (3H, $CH_3$), 2.30–2.42 m (1H, 3-$H_B$), 2.46 s (3H, $CH_3$), 2.69 s (3H, $SO_2CH_3$), 4.05 d.t (1H, 8b-H, $J_1$ = 8.4, $J_2$ = 9.1 Hz), 4.30 m (1H, 2-H), 5.05 q (1H, 3-$H_A$, $J$ = 8.4 Hz), 6.90 d (1H, $H_{arom}$, $J$ = 7.6 Hz), 7.03 d (1H, $H_{arom}$, $J$ = 7.6 Hz). Found, %: C 59.56; H 6.64; N 4.89; S 11.19. $C_{14}H_{19}NO_3S$. Calculated, %: C 59.76; H 6.81; N 4.98; S 11.40.

**Oxidation of alcohols IIa, III, V, and VIIIb** (*general procedure*)**.** A mixture of 0.48 g (1.6 mmol) of $K_2Cr_2O_7$, 0.6 ml of concentrated sulfuric acid, and 2.6 ml of water was added dropwise under stirring to a solution of 1.5 mmol of alcohol **IIa**, **III**, **V**, or **VIIIb** in 20 ml of acetone, and the mixture was stirred for 6 h at room temperature. When the reaction was complete, the mixture was treated with $NaHCO_3$ until carbon dioxide no longer evolved and was diluted with 50 ml of methylene chloride. The organic phase was washed with a 10% solution of $Na_2SO_3$ (2×30 ml) and water (2×50 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was recrystallized from carbon tetrachloride (compound **IV**) or ethanol (**VI**, **IX**).

**(4a*S*,9a*S*)-9-*p*-Tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-2-one (IVa).** Yield 0.34 g (66%), colorless crystals, mp 134–136°C. $^1$H NMR spectrum ($C_6D_6$), δ, ppm: 1.25–1.55 m (2H, 4-H), 1.70–1.78 m (2H, 3-H), 1.85 s (3H, $CH_3$), 2.63 d.d (1H, 1-$H_A$, $J_1$ = 7.0, $J_2$ = 16.0 Hz), 2.77 d.d (1H, 1-$H_B$, $J_1$ = 7.0, $J_2$ = 16.0 Hz), 2.78–2.87 m (1H, 4a-H), 4.29 d.t (1H, 9a-H, $J_1$ = 7.0, $J_2$ = 10.2 Hz), 6.58 d (1H, $H_{arom}$, $J$ = 7.4 Hz), 6.69 d (2H, $H_{arom}$, $J$ = 8.0 Hz), 6.76 t (1H, $H_{arom}$, $J$ = 7.2 Hz), 6.98 t (1H, $H_{arom}$, $J$ = 7.7 Hz), 7.51 t (2H, $H_{arom}$, $J$ = 8.0 Hz), 7.73 t (1H, $H_{arom}$, $J$ = 8.1 Hz). Found, %: C 66.68; H 5.42; N 3.99; S 9.11. $C_{19}H_{19}NO_3S$. Calculated, %: C 66.84; H 5.61; N 4.10; S 9.39.

**(2*R*,4a*S*,9a*R*)-2-Methoxy-8-methyl-9-*p*-tolylsulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-1-one (VI).** Yield 0.70 g (70%), colorless crystals, mp 117–119°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 0.85–2.30 m (4H, $CH_2$), 3.44 m (1H, 4a-H), 2.49 s (3H, $CH_3$), 2.63 s (3H, $CH_3$), 3.45 s (3H, $OCH_3$), 3.77 d.d (1H, 2-H, $J_1$ = 5.0, $J_2$ = 12.6 Hz), 5.00 d (1H, 9a-H, $J$ = 7.7 Hz), 6.80 d (1H, $H_{arom}$, $J$ = 6.0 Hz), 7.05–7.12 m (2H, $H_{arom}$), 7.37 d (2H, $H_{arom}$, $J$ = 8.1 Hz), 7.73 d (2H, $H_{arom}$, $J$ = 8.1 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 19.4, 21.5, 57.9 ($CH_3$); 21.9, 28.4 ($C^3$, $C^4$); 44.3 ($C^{4a}$); 73.1 ($C^{9a}$); 83.1 ($C^2$); 119.5, 126.7, 130.7 ($C^5$, $C^6$, $C^7$); 127.1, 129.5 ($C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 132.6, 135.8, 135.9, 141.9, 144.0 ($C^{8a}$, $C^8$, $C^{4b}$, $C^{1'}$, $C^{4'}$), 202.6 ($C^1$). Found, %: C 65.18; H 5.87; N 3.42; S 8.09. $C_{21}H_{23}NO_4S$. Calculated, %: C 65.43; H 6.01; N 3.63; S 8.32.

**(3a*S*,8b*S*)-5-Methyl-4-*p*-tolylsulfonyl-1,2,3,3a,-4,8b-hexahydrocyclopenta[*b*]indol-2-one (IX).** Yield 0.34 g (67%), colorless crystals, mp 150–152°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 d.d (1H, 3-$H_A$, $J$ = 8.0, $^2J$ = 20.0 Hz), 2.30–2.45 m (5H, $CH_3$, 1-$H_A$, 1-$H_B$), 2.60 s (3H, $CH_3$), 2.85 d.d (1H, 3-$H_B$, $J$ = 8.0, $^2J$ = 20.0 Hz), 2.95 m (1H, 8b-H), 4.95 q (1H, 3-$H_A$, $J$ = 8.0 Hz), 6.80 d (1H, $H_{arom}$, $J$ = 6.7 Hz), 7.10 m (4H, $H_{arom}$), 7.45 d (2H, $H_{arom}$, $J$ = 7.7 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 19.6, 21.4 ($CH_3$); 41.6 ($C^{8b}$); 42.3, 42.6 ($C^1$, $C^3$); 64.3 ($C^{3a}$); 122.1, 127.5, 127.7, 129.41, 131.1 ($C^6$, $C^7$, $C^8$, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 133.4, 133.9, 139.3, 140.0, 144.3 ($C^{4a}$, $C^5$, $C^{8a}$, $C^{1'}$, $C^{4'}$); 213.5 ($C^2$). Found, %: C 66.78; H 5.62; N 3.86; S 9.12. $C_{19}H_{19}NO_3S$. Calculated, %: C 66.84; H 5.61; N 4.10; S 9.39.

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