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Synthesis of New Partially Hydrogenated Carbazoles

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Abstract—Bromination of 2,5-dimethyl-, 2-methoxy-, and 2-methyl-6-(cyclohex-2-en-1-yl)-*N*-(*p*-tolylsulfonyl)anilines in the presence of a base gave the corresponding *N*-(*p*-tolylsulfonyl) derivatives of 1-bromo-, 1,5-dibromo-, and 1,6-dibromo-1,2,3,4,4a,9a-hexahydrocarbazoles which underwent dehydrobromination to 3,4,4a,9a-tetrahydrocarbazole derivatives on heating in piperidine.

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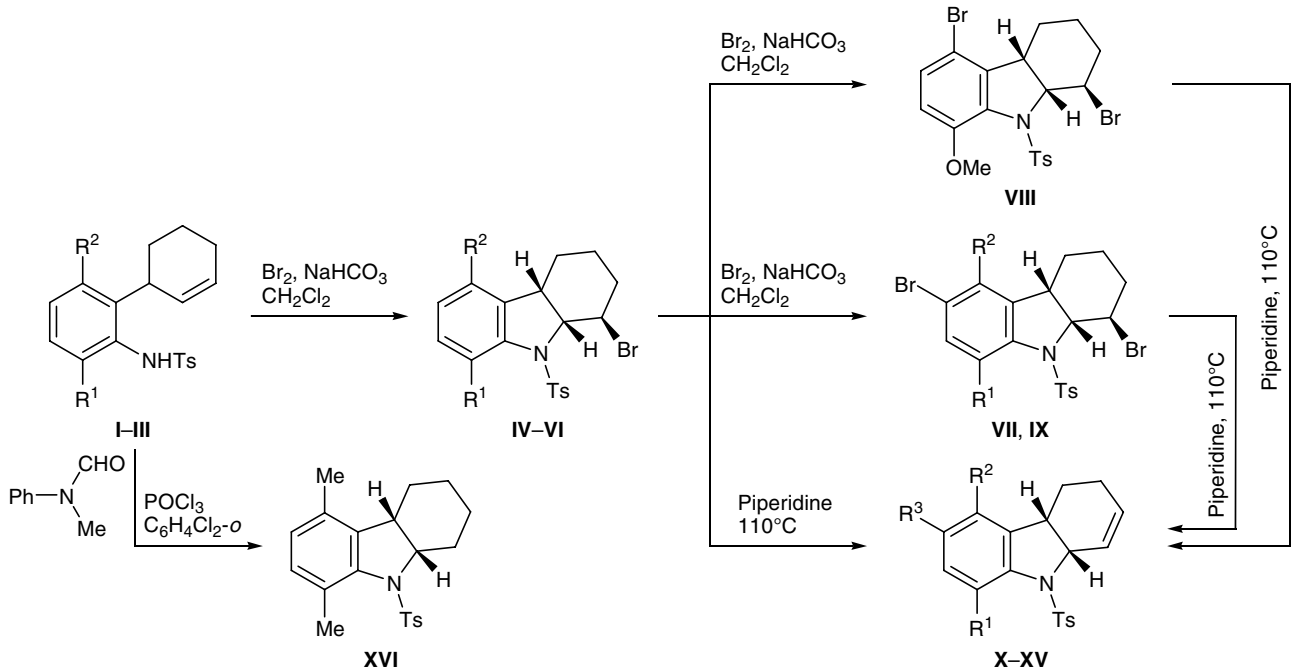
Alkaloids of the pyridocarbazole series [1, 2] exhibit antitumor activity; therefore, development of new methods for the synthesis of such heterocycles remains important up to now [3]. In most syntheses of this sort, carbazoles or their partially hydrogenated precursors are key intermediates. In the present work we made an attempt to synthesize partially hydrogenated 5,8-dimethyl-, 8-methyl-, and 8-methoxycarbazoles, as well as their 6- or 5-bromo derivatives from the corresponding 2-(cyclohex-2-en-1-yl)anilines [4].

1-Bromohexahydrocarbazoles **IV**–**VI** were obtained in almost quantitative yield by cyclization of *N*-(*p*-tolylsulfonyl)anilines **I**–**III** by the action of bromine in the presence of sodium hydrogen carbonate. The subsequent bromination of **IV** gave compound **VII** as a result of electrophilic replacement of hydro-

Scheme 1.



I, **IV**, **VII**, **X**, **XIII**; $R^1 = R^2 = Me$; **III**, **VI**, **IX**, **XII**, **XV**, $R^1 = Me$, $R^2 = H$; **II**, **V**, **XI**, $R^1 = MeO$, $R^2 = H$; **XIV**, $R^1 = MeO$, $R^2 = Br$; **X**–**XII**, **XIV**, $R^3 = H$; **XIII**, **XV**, $R^3 = Br$.

gen on C^6 by bromine. An analogous reaction of **V** with Br_2 afforded 5-bromo derivative **VIII** as the major product. The position of the halogen atom was determined on the basis of the ^1H NMR data. In the ^1H NMR spectrum of dibromide **VIII**, the 6-H and 7-H protons resonated as two doublets at δ 6.68 and 7.22 ppm with a coupling constant *J* of 8.9 Hz. Two two-proton doublets were assigned to the *p*-tolylsulfonyl group (δ 7.30 and 7.98 ppm). Presumably, the minor product is the corresponding 7-bromo isomer.

When a mixture of hexahydrocarbazole **VI** with Br_2 in methylene chloride was stirred on exposure to light, it turned colorless, presumably as a result of bromination of the solvent. After appropriate treatment, the initial compound was recovered from the reaction mixture. We succeeded in obtaining compound **IX** by bromination of **VI** in the dark. The position of bromine at C^6 was determined on the basis of the ^1H NMR spectrum which contained two one-proton singlets at δ 6.92 and 7.30 ppm belonging to 5-H and 7-H. On heating in piperidine, compounds **IV**–**IX** underwent dehydrohalogenation to tetrahydrocarbazoles **X**–**XV**.

Our attempt to effect formylation of *N*-(*p*-tolylsulfonyl)aniline **I** at the *para* position with respect to the amino group by heating with *N*-methyl-*N*-phenylformamide in dichlorobenzene in the presence of $POCl_3$ resulted in the formation of hexahydrocarbazole **XVI** as the only product; compound **XVI** is used as intermediate product in some syntheses [5] of Ellipticine. The cyclohexene ring in molecule **I** contains no functional groups which could favor introduction of other substituents.

The upfield regions of the ^1H NMR spectra of compounds **IV** and **VII** are almost similar. The doublet of doublets from 9a-H in the spectra of **IV**–**IX** is characterized by two large coupling constants, indicating nearly axial orientation of that proton ($J_{9a,1} \approx 9$–10 Hz) and *cis*-junction of the cyclohexane and pyrrole rings ($J_{9a,4a}$ = 6.4–6.7 Hz). The axial orientation of 1-H also follows from the corresponding large coupling constants $J_{9a,1} \approx 9$–10 Hz and $J_{1,2\text{-}ax} \approx 12$ Hz, while the small coupling constant $J_{1,2\text{-}eq}$ = 4.5–5.0 Hz suggests interaction between 1-H and 2-H_{eq}. The 4a-H is likely to occupy equatorial position, for it is not characterized by large coupling constants, and its signal appears in the ^1H NMR spectrum as a poorly resolved multiplet. The 6-H and 7-H protons in the aromatic ring of **IV** resonate as two one-proton singlets. In the ^1H NMR spectrum of **VII** only a singlet at δ 7.37 ppm (7-H) is present. In addition, the multiplicity of aromatic carbon signals in the ^{13}C NMR spectrum of **VII** differs from that observed in the spectrum of initial monobromo derivative **IV** [6].

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded from solution in $CDCl_3$ on a Bruker AM-300 instrument operating at 300.13 and 75.45 MHz, respectively; the chemical shifts were measured relative to tetramethylsilane as internal reference. The elemental compositions were determined on an M-185B CHN Analyzer. Column chromatography was performed on silica gel (40–70 μm; Lancaster). Silica gel plates (*Lyuminofor*, Russia) were used for qualitative TLC analysis; spots were visualized under UV light (λ 254 nm) or by treatment with iodine vapor. The melting points were determined on a Boetius melting point apparatus.

***N*-[2-(Cyclohex-2-en-1-yl)-3,6-dimethylphenyl]-*p*-toluenesulfonamide (I).** *p*-Toluenesulfonyl chloride, 3.09 g (15 mmol), was added at room temperature to a solution of 2 g (10 mmol) of 2-(cyclohex-2-en-1-yl)-2,5-dimethylaniline [4] in 15 ml of pyridine. After 24 h, the mixture was diluted with 20 ml of H_2O, stirred for 30 min, and evaporated under reduced pressure. The residue was dissolved in 40 ml of chloroform, the solution was washed with water (2×20 ml), 10% aqueous $NaHCO_3$ (20 ml), and water again (20 ml) and dried over Na_2SO_4, the solvent was removed under reduced pressure, and crude product **I**, 3.45 g (98%), was recrystallized from ethanol. Yield 3.36 g (96%), mp 190–193°C (from EtOH). ^1H NMR spectrum, δ, ppm: 1.39–2.22 m (6H, CH_2); 1.98 s, 2.32 s, and 2.45 s (3H each, CH_3); 3.98 m (1H, 1'-H); 5.58 m (2H, 2'-H, 3'-H); 6.92 d (1H, 4-H); 6.98 d (1H, 5-H); 7.27 d (2H, 3"-H, 5"-H, *J* = 8.2 Hz); 7.69 d (2H, 2"-H, 6"-H, *J* = 8.2 Hz). Found, %: C 70.67; H 6.82; N 3.73; S 8.76. $C_{21}H_{25}NO_2S$. Calculated, %: C 70.95; H 7.09; N 3.94; S 9.02.

Compounds **II** and **III** were synthesized in a similar way.

***N*-[2-(Cyclohex-2-en-1-yl)-6-methoxyphenyl]-*p*-toluenesulfonamide (II)** was obtained from 5 g (25 mmol) of 2-(cyclohex-2-en-1-yl)-6-methoxyaniline. Yield 8.56 g (96%), mp 178–180°C (from EtOH). ^1H NMR spectrum, δ, ppm: 1.25–2.15 m (6H, CH_2), 2.40 s (3H, CH_3), 3.15 s (3H, OCH_3), 4.35 m (1H, 1'-H), 5.60–5.88 m (2H, 2'-H, 3'-H), 6.15 s (1H, NH), 6.47 d.d (1H, 5-H, J_1 = 1.2, J_2 = 8.2 Hz), 6.94 d.d (1H, 3-H, J_1 = 1.2, J_2 = 8.0 Hz), 7.18 m (3H, H_{arom}),

7.51 d (2H, 2"-H, 6"-H, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.3 (CH_3); 21.5, 24.8, 31.3 ($C^{4'}$, $C^{5'}$, $C^{6'}$); 36.3 ($C^{1'}$); 54.5 (OCH_3); 107.7 (C^5); 121.0, 128.1, 128.9, 130.7 (C^3, C^4, $C^{2'}$, $C^{3'}$); 127.5, 128.6 ($C^{2"}$, $C^{6"}$, $C^{3"}$, $C^{5"}$); 122.2, 136.6, 143.0, 147.2 (C^1, C^2, $C^{1"}$, $C^{4"}$); 153.9 (C^6). Found, %: C 67.18; H 6.57; N 4.00; S 8.82. $C_{20}H_{23}NO_3S$. Calculated, %: C 67.20; H 6.49; N 3.92; S 8.97.

***N*-[2-(Cyclohex-2-en-1-yl)-6-methylphenyl]-*p*-toluenesulfonamide (III)** was obtained from 5 g (26.9 mmol) of 2-(cyclohex-2-en-1-yl)-6-methylaniline. Yield 8.23 g (90%), mp 169–170°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.25–2.50 m (6H, CH_2), 2.10 s and 2.40 s (3H each, CH_3), 3.47 m (1H, 1'-H), 5.24 m (1H, 2'-H), 5.75 m (1H, 3'-H), 6.05 s (1H, NH), 7.05–7.26 m (5H, H_{arom}), 7.60 d (2H, 2"-H, 6"-H, J = 8.3 Hz). Found, %: C 70.18; H 6.57; N 4.05; S 9.52. $C_{20}H_{23}NO_2S$. Calculated, %: C 70.35; H 6.79; N 4.10; S 9.39.

***N*-(1-Bromo-5,8-dimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (IV).** A solution of 0.48 g (3 mmol) of bromine in 1 ml of methylene chloride was added dropwise under stirring to a solution of 1 g (3 mmol) of compound **I** in 10 ml of methylene chloride. The mixture was stirred for 18 h at 20°C (the progress of the reaction was monitored by TLC), diluted with 50 ml of methylene chloride, and washed with a 10% solution of $NaHCO_3$ (2×20 ml) and water (2×50 ml). The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Yield 0.99 g (82.5%), mp 203–206°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.00–2.50 m (6H, CH_2), 2.10 s (3H, CH_3), 2.40 s (3H, CH_3), 2.55 s (3H, CH_3), 3.12 m (1H, 4a-H), 3.70 d.d.d (1H, 1-H, J_1 = 4.8, J_2 = 9.7, J_3 = 12.8 Hz), 4.35 d.d (1H, 9a-H, J_1 = 6.4, J_2 = 9.7 Hz), 6.85 d (1H, H_{arom}, J = 7.8 Hz), 7.02 d (1H, H_{arom}, J = 7.8 Hz), 7.18 d (2H, H_{arom}, J = 8.2 Hz), 7.57 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.0, 19.2, 21.4 (CH_3); 22.0, 24.5, 35.7 (CH_2); 43.8 (C^{4a}); 51.5 (C^1); 71.9 (C^{9a}); 127.6, 129.2, 129.6, 129.9 (C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 130.8, 131.4, 135.2, 135.6, 141.1, 143.9 (C^{4b}, C^5, C^8, C^{8a}, $C^{1'}$, $C^{4'}$). Found, %: C 57.84; H 5.24; Br 17.91; N 2.87; S 7.01. $C_{21}H_{24}BrNO_2S$. Calculated, %: C 58.07; H 5.57; Br 18.40; N 3.22; S 7.40.

Compounds **V** and **VI** were synthesized in a similar way.

***N*-(1-Bromo-8-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (V)** was obtained from 1 g (2.8 mmol) of compound **II**. Yield 0.98 g (80%), mp 176–177°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.10–2.30 m (6H, CH_2), 2.43 s (3H, CH_3), 3.60–3.75 m (2H, 1-H, 4a-H), 3.76 s (3H, OCH_3), 4.90 d.d (1H, 9a-H, J_1 = 6.7, J_2 = 9.7 Hz), 6.70 d (1H, 7-H, J = 7.5 Hz), 6.80 d (1H, 5-H, J = 7.2 Hz), 7.15 d.d (1H, 6-H, J_1 = 7.2, J_2 = 7.5 Hz), 7.30 d (2H, 3'-H, 5'-H, J = 8.3 Hz), 8.0 d (3H, 2'-H, 6'-H, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.5 (CH_3); 22.2, 23.9 (C^3, C^4); 36.3 (C^2); 44.3 (C^{4a}); 52.5 (C^1); 55.7 (OCH_3); 73.3 (C^{9a}); 112.1, 115.0, 127.4 (C^5, C^6, C^7); 128.2 ($C^{3'}$, $C^{5'}$); 128.6 ($C^{2'}$, $C^{6'}$); 130.6, 137.9, 139.2, 143.3 (C^{4b}, $C^{1'}$, C^{8a}, $C^{4'}$); 152.6 (C^8). Found, %: C 55.15; H 5.02; Br 18.41; N 3.28; S 7.23. $C_{20}H_{22}BrNO_3S$. Calculated, %: C 55.05; H 5.08; Br 18.31; N 3.21; S 7.35.

***N*-(1-Bromo-8-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (VI)** was obtained from 1.0 g (2.9 mmol) of compound **III**. Yield 1.17 g (96%), mp 215–220°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.00–2.30 m (6H, CH_2), 2.40 s (3H, CH_3), 2.60 s (3H, CH_3), 2.75 m (1H, 4a-H), 3.72 d.d.d (1H, 1-H, J_1 = 4.0, J_2 = 10.2, J_3 = 13.5 Hz), 4.53 d.d (1H, 9a-H, J_1 = 6.5, J_2 = 10.2 Hz), 6.80 d (1H, 7-H, J = 7.0 Hz), 7.06–7.15 m (2H, 5-H, 6-H), 7.18 d (2H, 3'-H, 5'-H, J = 8.1 Hz), 7.55 d (2H, 3'-H, 6'-H, J = 8.1 Hz). Found, %: C 57.03; H 5.22; Br 19.41; N 3.28; S 7.83. $C_{20}H_{22}BrNO_2S$. Calculated, %: C 57.15; H 5.27; Br 19.01; N 3.33; S 7.63.

***N*-(1,6-Dibromo-5,8-dimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (VII).** A solution of 0.08 g (0.5 mmol) of bromine in 1 ml of methylene chloride was added dropwise under stirring to a solution of 0.2 g (0.5 mmol) of compound **IV** in 10 ml of methylene chloride. The mixture was stirred for 18 h at 20°C (TLC), diluted with 50 ml of methylene chloride, and washed with a 10% solution of $NaHCO_3$ (2×20 ml) and water (2×50 ml). The organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.22 g (95%), mp 143–145°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 0.95–2.40 m (6H, CH_2), 2.23 s (3H, CH_3), 2.43 s (3H, CH_3), 2.49 s (3H, CH_3), 3.20 m (1H, 4a-H), 3.69 d.d.d (1H, 1-H, J_1 = 5.0, J_2 = 9.7, J_3 = 12.5 Hz), 4.33 d.d (1H, 9a-H, J_1 = 6.5, J_2 = 9.7 Hz), 7.23 d (2H, H_{arom}, J = 8.1 Hz), 7.37 s (1H, 7-H), 7.59 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.8, 19.1, 21.6 (CH_3); 22.0, 24.9 (C^3, C^4); 35.6 (C^2); 44.7 (C^{4a}); 51.2 (C^1); 71.8 (C^{9a}); 127.9, 129.4, 133.9 (C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 123.8, 131.3, 132.6, 135.4, 137.6, 140.8, 144.3 (C^{4b}, C^5, C^6, C^8, C^{8b}, $C^{1'}$, $C^{4'}$). Found, %: C 48.79;

H 4.22; Br 30.83; N 2.36; S 5.89. $C_{21}H_{23}Br_2NO_2S$. Calculated, %: C 49.14; H 4.52; Br 31.13; N 2.73; S 6.25.

Compounds **VIII** and **IX** were synthesized in a similar way.

***N*-(1,5-Dibromo-8-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (VIII)** was obtained from 0.5 g (1.15 mmol) of compound **V**. Yield 0.48 g (81%), mp 129–132°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.25–2.30 m (6H, CH_2), 2.40 s (3H, CH_3), 3.10 m (1H, 4a-H), 3.65 s (3H, OCH_3), 3.60–3.75 m (1H, 1-H), 4.80 d.d (1H, 9a-H, J_1 = 6.4, J_2 = 9.4 Hz), 6.80 d (1H, H_{arom}, J = 8.8 Hz), 7.20 d (1H, H_{arom}, J = 8.8 Hz), 7.30 d (2H, H_{arom}, J = 8.3 Hz), 7.95 d (1H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.5, 55.7 (CH_3); 22.0, 24.0 (C^3, C^4); 35.7 (C^2); 47.4 (C^{4a}); 52.2 (C^1); 72.3 (C^{9a}); 108.1, 133.3, 136.1, 137.7, 143.4, 151.6 (C^{4b}, C^5, C^8, C^{8a}, $C^{1'}$, $C^{4'}$); 113.6, 128.1, 128.7, 131.6 (C^5, C^6, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$). Found, %: C 46.32; H 4.18; Br 30.98; N 2.65; S 6.34. $C_{20}H_{21}Br_2NO_3S$. Calculated, %: C 46.62; H 4.11; Br 31.01; N 2.72; S 6.22.

***N*-(1,6-Dibromo-8-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (IX)** was obtained from 0.5 g (1.2 mmol) of compound **VI**; the reaction was carried out in the dark. Yield 0.19 g (32%), mp 203–205°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.52–1.8 m (6H, CH_2), 2.43 s and 2.58 s (3H each, CH_3), 2.92 m (1H, 4a-H), 4.42 d.d (1H, 9a-H, J_1 = 2.7, J_2 = 6.7 Hz), 6.92 d (1H, H_{arom}), 7.22 d (2H, H_{arom}, J = 8.1 Hz), 7.30 s (1H, H_{arom}), 7.61 d (2H, H_{arom}, J = 8.1 Hz). Found, %: C 48.32; H 4.18; Br 31.98; N 2.65; S 6.34. $C_{20}H_{21}Br_2NO_2S$. Calculated, %: C 48.16; H 4.24; Br 32.01; N 2.81; S 6.42.

***N*-(5,8-Dimethyl-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (X).** A solution of 0.57 g (1 mmol) of compound **IV** in 10 ml of piperidine was heated for 6 h at 110°C. When the dehydrobromination was complete, the solvent was removed under reduced pressure, the residue was dissolved in 50 ml of methylene chloride, and the solution was washed with water (2×20 ml). The organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure, and crude product **X** was recrystallized from ethanol. Yield 0.36 g (77.5%), mp 118–121°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.55–1.82 m (4H, CH_2); 2.11 s, 2.48 s, and 2.50 s (3H each, CH_3); 2.64 m (1H, 4a-H); 4.77 d (1H, 9a-H, J = 7.8 Hz); 5.60 m and 5.78 m (2H, 1-H, 2-H); 6.84 d (1H, 6-H, J = 7.7 Hz); 7.01 d (1H, 7-H, J = 7.6 Hz); 7.15 d (2H, 3'-H, 5'-H, J = 8.1 Hz), 7.34 d (2H, 2'-H, 6'-H, J = 9.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.8, 19.5, 20.1 (CH_3); 21.6, 22.8 (CH_2); 43.6 (C^{4a}); 71.5 (C^{9a}); 126.4, 127.7, 128.6, 129.3, 130.1, 131.5 (C^1, C^2, C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 130.4, 131.4, 135.2, 136.3, 141.5, 143.8 (C^{4b}, C^5, C^8, C^{8a}, $C^{1'}$, $C^{4'}$). Found, %: C 71.07; H 6.19; N 3.64; S 8.81. $C_{21}H_{23}NO_2S$. Calculated, %: C 71.40; H 6.56; N 3.90; S 9.07.

Compounds **XI**–**XV** were synthesized in a similar way.

***N*-(8-Methoxy-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XI)** was obtained from 1.3 g (3 mmol) of compound **V**. Yield 0.98 g (92%), mp 151–153°C. ^{1}H NMR spectrum, δ, ppm: 1.65–2.10 m (4H, CH_2), 2.40 s (3H, CH_3), 3.05 m (1H, 4a-H), 3.82 s (3H, OCH_3), 5.08 d (1H, 9a-H, J = 7.3 Hz), 5.70 d (1H, 1-H, J = 10.3 Hz), 6.68 d (1H, 2-H, J = 7.3 Hz), 6.82 d (1H, 5-H, J = 8.2 Hz), 7.10–7.28 m (4H, H_{arom}), 7.60 d (2'-H, 5'-H, J = 8.2 Hz). Found, %: C 67.49; H 5.80; N 4.05; S 9.18. $C_{20}H_{21}NO_3S$. Calculated, %: C 67.58; H 5.95; N 3.94; S 9.02.

***N*-(8-Methyl-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XII)** was obtained from 0.4 g (0.8 mmol) of compound **VI**. Yield 0.285 g (98%), mp 168–170°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.60–1.95 m (4H, CH_2), 2.40 s (3H, CH_3), 2.60 s (3H, CH_3), 2.50–2.62 m (1H, 4a-H), 4.83 d.d.d (1H, 9a-H, J_1 = 1.9, J_2 = 4.6, J_3 = 7.0 Hz), 5.65 d.t (1H, 2-H, J_1 = 2.8, J_2 = 10.2 Hz), 5.96 d.d (1H, 1-H, J_1 = 5.0, J_2 = 10.2 Hz), 6.81 d (1H, 5-H, J = 5.6 Hz), 7.05–7.20 m (4H, H_{arom}), 7.41 d (2H, 2'-H, 5'-H, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.1, 21.5 (CH_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 70.91; H 6.12; N 4.45; S 9.36. $C_{20}H_{21}NO_2S$. Calculated, %: C 70.77; H 6.24; N 4.13; S 9.44.

***N*-(6-Bromo-5,8-dimethyl-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XIII)** was obtained from 0.7 g (2 mmol) of dibromide **VII**. Yield 0.49 g (85%), mp 210–212°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.48–1.98 m (4H, CH_2); 2.19 s, 2.43 s, and 2.49 s (3H each, CH_3); 3.15 m (1H, 4a-H); 4.75 d.t (1H, 9a-H); 5.59 d.t (1H, 2-H, J = 2.0 Hz); 5.80 d.d (1H, 1-H, J_1 = 1.3, J_2 = 4.0 Hz); 7.18 d (2H, 2'-H, 6'-H, J = 7.5 Hz); 7.27 s (1H, 7-H); 7.35 d (2H, 3'-H, 5'-H, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.4, 18.9, 21.4 (CH_3); 19.8, 22.2 (CH_2); 39.6 (C^{4a});

62.9 (C^{9a}); 122.8 (C^6); 125.8 (C^1); 127.3 (C^2); 129.1 ($C^{2'}$, $C^{6'}$); 131.0 (C^8); 131.3 ($C^{3'}$, $C^{5'}$); 131.7 (C^5); 133.5 (C^7); 134.5 (C^{4b}); 138.2 (C^{8a}); 140.7 ($C^{1'}$); 143.9 ($C^{4'}$). Found, %: C 58.32; H 5.11; Br 18.47; N 3.21; S 7.38. $C_{21}H_{22}BrNO_2S$. Calculated, %: C 58.34; H 5.13; Br 18.48; N 3.24; S 7.41.

***N*-(5-Bromo-8-methoxy-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XIV)** was obtained from 0.2 g (0.38 mmol) of compound **VIII**. Yield 0.15 g (91%), amorphous substance, R_f 0.72 (C_6H_6–EtOAc, 5:1). ^{1}H NMR spectrum, δ, ppm: 1.30–2.30 m (4H, CH_2), 2.50 s (3H, CH_3), 3.30 m (1H, 4a-H), 3.70 s (3H, OCH_3), 5.05 d (1H, 9a-H, J = 6.2 Hz), 5.70–5.95 m (2H, 1-H, 2-H), 6.65 d (1H, 7-H, J = 8.7 Hz), 7.15 d (1H, 6-H, J = 8.7 Hz), 7.20 d (2H, 3'-H, 5'-H, J = 8.2 Hz), 7.69 d (2H, 2'-H, 6'-H, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 22.6 (C^3, C^4); 21.4 (CH_3); 41.7 (C^{4a}); 55.7 (OCH_3); 62.3 (C^{9a}); 109.5 (C^5); 132.7, 137.3, 137.8, 143.3 (C^{4b}, C^{8a}, $C^{1'}$, $C^{4'}$); 150.7 (C^8); 113.6 (C^7); 125.5, 127.1, 129.1, 130.2, 132.1 (C^6, C^1, C^2, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$). Found, %: C 55.10; H 4.50; Br 18.34; N 3.45; S 7.45. $C_{20}H_{20}BrNO_3S$. Calculated, %: C 55.31; H 4.64; Br 18.40; N 3.22; S 7.38.

***N*-(6-Bromo-8-methyl-3,4,4a,9a-tetrahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XV)** was obtained from 0.12 g (0.2 mmol) of dibromo derivative **IX**. Yield 0.06 g (71%), mp 161–163°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 1.50–2.00 m (4H, CH_2), 2.40 s (3H, CH_3), 2.51 s (3H, CH_3), 2.52–2.61 m (1H, 4a-H), 4.70 d.d.d (1H, 9a-H, J_1 = 2.0, J_2 = 4.6, J_3 = 7.0 Hz), 5.60 m (1H, 2-H), 5.57 m (1H, 1-H), 6.94 s (1H, H_{arom}), 7.20 d (2H, H_{arom}, J = 8.3 Hz), 7.25 s (1H, H_{arom}), 7.45 d (2H, H_{arom}, J = 8.3 Hz). Found, %: C 57.10; H 4.50; Br 18.94; N 3.45; S 7.45. $C_{20}H_{20}BrNO_2S$. Calculated, %: C 57.42; H 4.82; Br 19.10; N 3.35; S 7.66.

***N*-(5,8-Dimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-*p*-toluenesulfonamide (XVI).** *N*-Methyl-*N*-phenylformamide, 0.29 g (2 mmol), and phosphoryl chloride, 0.274 ml (2 mmol), were dissolved in 10 ml of dichlorobenzene on heating, 0.763 g (2 mmol) of compound **I** was added under stirring, and the mixture was heated for 10 h at 100°C. When the reaction was complete, the solvent was removed under reduced pressure, the residue was dissolved in chloroform, the solution was washed with 100 ml of a 10% solution of $NaHCO_3$, the organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subjected to chromatography in a short column charged with silica gel using benzene as eluent. Yield 0.586 g (76.8%), amorphous substance, R_f 0.6 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum, δ, ppm: 1.20–1.62 m (8H, CH_2); 2.12 s, 2.43 s, and 2.52 s (3H each, CH_3); 2.63 m (1H, 4a-H); 4.2 m (1H, 9a-H); 6.82 d (1H, 6-H, J = 7.8 Hz); 6.98 d (1H, 7-H, J = 7.8 Hz); 7.16 d (2H, 3'-H, 5'-H, J = 8.1 Hz); 7.41 d (2H, 2'-H, 6'-H, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.0, 19.3, 21.3 (CH_3); 20.3, 22.6, 24.9, 27.8 (CH_2); 40.8 (C^{4a}); 63.9 (C^{9a}); 127.1, 128.7, 129.1, 129.6 (C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 130.0, 131.5, 135.8, 136.6, 141.0, 143.5 (C^{4b}, C^5, C^6, C^8, C^{8a}, $C^{1'}$, $C^{4'}$). Found, %: C 69.86; H 6.85; N 3.65; S 8.75. $C_{21}H_{25}NO_2S$. Calculated, %: C 70.90; H 7.09; N 3.94; S 9.02.

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