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Reactions of *N*- and C-Alkenylanilines: V.* Synthesis of Iodo-Substituted Heterocycles from *o*-Cycloalkenylanilines and Their Transformations

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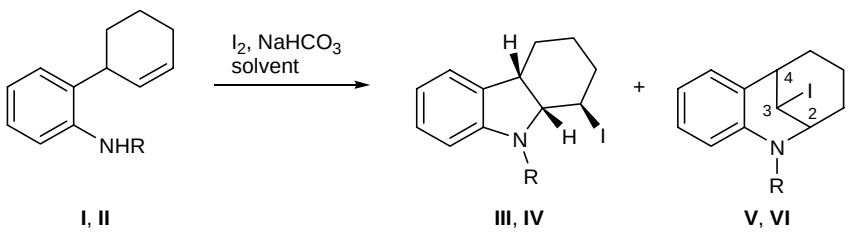
Abstract—Iodination of *N*-isopropyl- and *N*-benzyl-2-(2-cyclohexenyl)anilines gave the corresponding 1-iodohexahydrocarbazoles which underwent quantitative isomerization into 3-iodo-2,4-propano-1,2,3,4-tetrahydroquinolines. Nucleophilic substitution in 1-iodohexahydrocarbazoles and 3-iodo-2,4-propano-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole was studied. N-Allylation of the latter via reaction with allyl bromide is accompanied by replacement of the iodine atom by bromine.

Interest in compounds of the cyclohexa- and cyclopenta[*b*]indole series arises primarily from the fact that they constitute structural fragments of some alkaloids [2] and are used in the synthesis of biologically active substances [3]. The first synthesis of a compound of the above series was described in [4]. In continuation of our studies on cyclization of *o*-cycloalkenylanilines [5, 6], in the present work we examined the cyclization of *N*-isopropyl- and *N*-benzyl-2-(2-cyclohexenyl)-anilines **I** and **II** by the action of iodine and nucleophilic substitution of the halogen atom in the resulting 1-iodohexahydrocarbazoles **III** and **IV**. Also, analogous transformations of previously synthesized 3-iodohexahydrocyclopenta[*b*]indole were studied [5].

We showed in [6] that cyclization of cyclohexenylanilines having no substituent on the nitrogen group by the action of iodine takes different pathways, depending on the solvent. Analogous reaction of N-substituted amines **I** and **II** with I_2 in CCl_4 in the presence of $NaHCO_3$ leads to hexahydrocarbazoles **III** and **IV** (Scheme 1). The selectivity decreases in going to other solvents, such as methylene chloride and acetonitrile. Here, the reactions are accompanied by *endo*-6-cyclization and intramolecular isomerization of carbazoles **III** and **IV** into tetrahydroquinoline derivatives **V** and **VI**. The latter were the only products obtained from compounds **I** and **II** in acetonitrile. Heterocycles **III** and **IV** in acetonitrile or chloroform were converted into tetrahydroquinolines **V** and **VI**, respectively, at different rates. By measuring intensities of proton signals in the ^1H NMR spectra in $CDCl_3$ we found that the isomerization of *N*-isopropylcar-

Scheme 1.



I, **II** **III**, **IV** **V**, **VI**

I, **III**, **V**, R = *i*-Pr ; **II**, **IV**, **VI**, R = $PhCH_2$.

* For communication IV, see [1].

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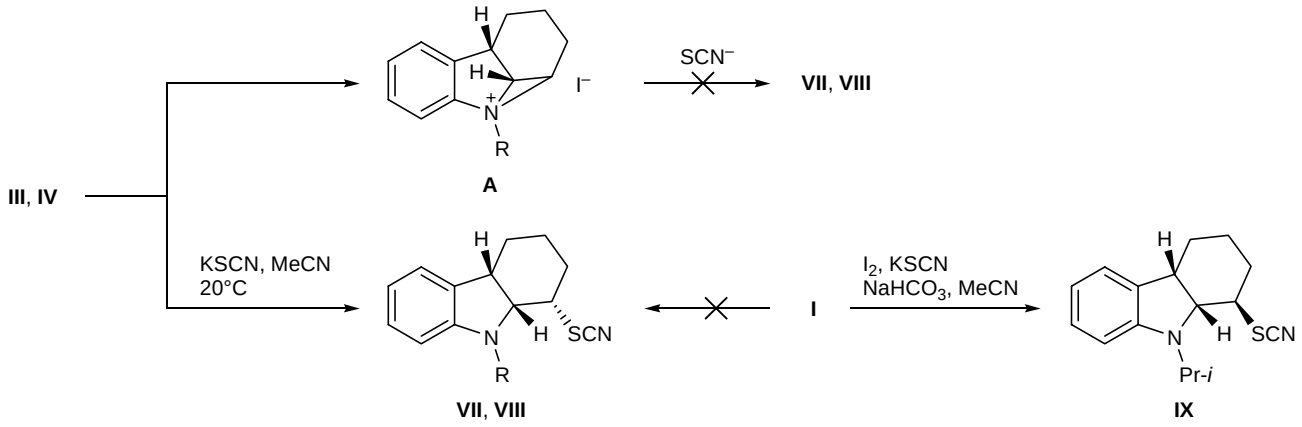
Scheme 2.



VII, R = *i*-Pr; **VIII**, R = $PhCH_2$.

bazole **III** into **V** is faster than the isomerization of its *N*-benzyl analog **IV**.

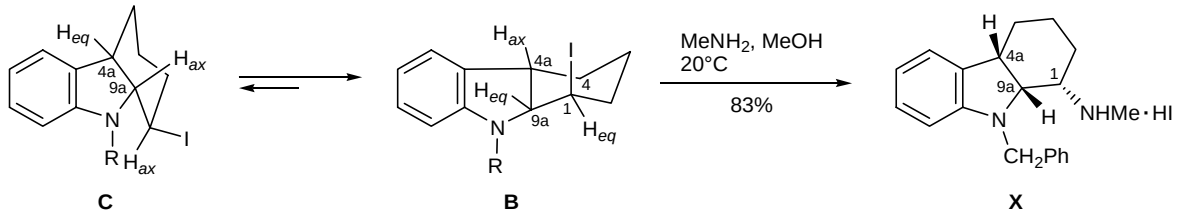
No expansion of the indole ring into quinoline occurred when potassium thiocyanate (which is readily soluble in acetonitrile) was added to a solution of carbazole **III** and **IV**, and the corresponding 1-thiocyanato derivatives **VII** and **VIII** were obtained in almost quantitative yield (Scheme 2). Thiocyanates **VII** and **VIII** cannot be formed by transformation of aziridinium salt **A**, for in this case orientation of the substituent on C^1 would be the opposite. The reaction of amine **I** with I_2 in acetonitrile in the presence of KSCN and $NaHCO_3$ gave compound **IX** which is stereoisomeric to **VII**. Presumably, it was formed via direct reaction of **I** with $(SCN)_2$.

The NMR spectra of compounds **VII** and **IX** differ only slightly. The ^{13}C NMR spectrum of a mixture of **VII** and **IX** contained a double set of signals. The C^{9a}–H and C^1–S bonds in **VII** are arranged *cis*; in keeping with the known rule for 1,2- or 1,3-*syn* arrangement of substituents, the corresponding carbon signals shift upfield.

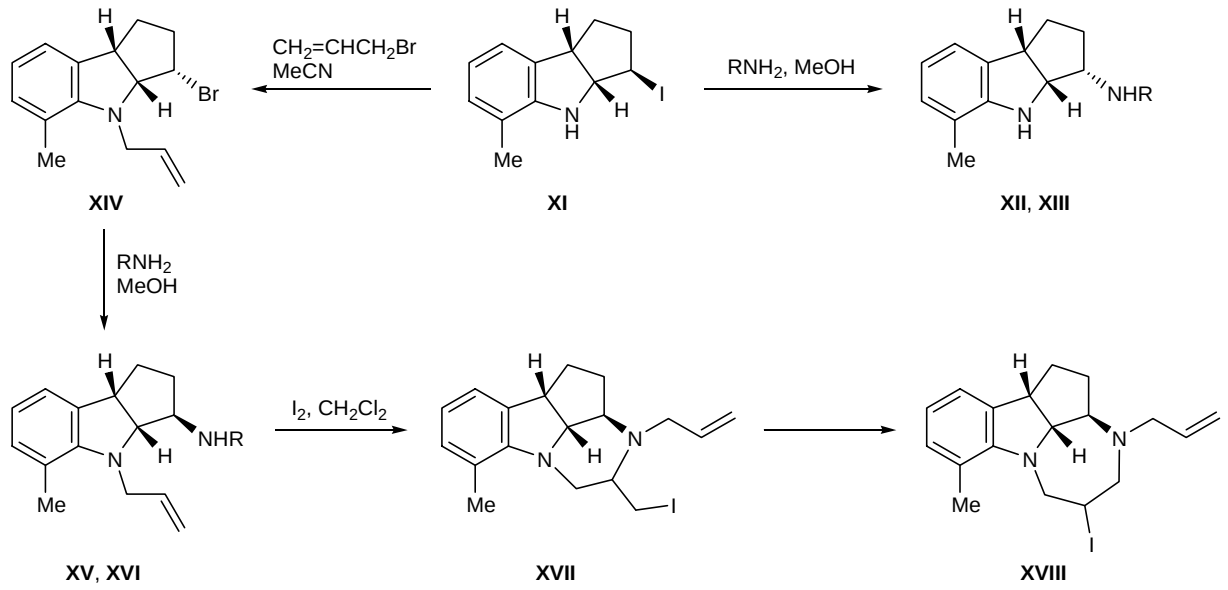
The coupling constant between the 1-H and 9a-H protons in the ^1H NMR spectrum of hydroiodide **X** (which was obtained by reaction of hexahydrocarbazole **IV** with methylamine in methanol; Scheme 3) indicates that the former is axial and that the latter is equatorial. A strong effect of the N-substituent on the conformation was observed for 1-iodohexahydrocarbazoles **III** and **IV**. The cyclohexane fragment in hexahydrocarbazoles **III** and **IV** in solution has a *chair* conformation (**B**) where the 1-H and 9a-H protons are equatorial. This follows from the small coupling constant $J_{1,9a}$ = 2–4 Hz. The large coupling constant observed for 9a-H and 4a-H (J = 6.4–7.1 Hz) indicates *cis*-junction of the rings [7]. Substituent on the nitrogen atom is likely to favor displacement of conformational equilibrium of hexahydrocarbazoles **III** and **IV** toward the above form. Hexahydrocarbazoles having no N-alkyl substituent [9, 10] were found to exist as conformers **C**. We recorded the ^1H NMR spectra of compound **IV** at 20 and 50°C. Raising the temperature resulted in some increase of the fraction of conformer **C**, as followed from increase in the coupling constant $J_{1,9a}$ from 2.4 to 2.7 Hz and decrease in $J_{4a,4\text{-}ax}$ from 11.0 to 10.8 Hz.

A substituent can be introduced to the nitrogen atom both before and after heterocyclization of alkenylaniline. Moreover, taking into account different properties of the nitrogen- and halogen-containing

Scheme 3.



Scheme 4.



XII, **XV**, R = H; **XIII**, **XVI**, R = CH_2=$CHCH_2$.

moieties, either alkenylation of the amino group or replacement of the halogen atom by alkenylamino group can be effected. For example, cyclopenta[*b*]-indole **XI** reacted with ammonia in acetonitrile at 100°C to give diamine **XII** [5] (Scheme 4). The replacement of iodine by allylamino group occurs at room temperature with formation of 3-allylamino-indole **XIII** in high yield. The allylation of **XI** with allyl bromide in acetonitrile was accompanied by replacement of the iodine atom by bromine to afford 3-bromoindole **XIV** with a different configuration at C^3. By reaction of **XIV** with ammonia or allylamine we obtained diamines **XV** and **XVI**, respectively, the configuration at C^3 remaining unchanged (Scheme 4). Diallyl derivative **XVI** reacted with I_2 to give heterocycle **XVII** which underwent fast rearrangement into seven-membered isomer **XVIII**.

The structure of 3-bromocylopenta[*b*]indole **XIV** was proved by elemental analysis and spectral data. The JMOD ^{13}C NMR spectrum of **XIV** contained 7 signals in the aliphatic region; among these, the doublet at δ_C 58.4 ppm was assigned to the C^3 atom [7]. Compound **XIV** showed in the mass spectrum the molecular ion peak with *m*/*z* 291, and strong peaks with *m*/*z* 212 $[M - Br]^+$ (base peak), 184 $[M - Br - C_2H_4]^+$, and 170 $[M - Br - C_6H_6]^+$ were present. Assuming that the replacement of iodine in **XI** follows the S_N2 mechanism, the 3-H and 3a-H protons in **XIV** should be arranged *cis*.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C); chloroform-*d* was used as solvent, and tetramethylsilane, as internal reference. The IR spectra were measured on a UR-20 instrument. The purity of initial amines **I** and **II** was checked by GLC on a Chrom-5 chromatograph equipped with a flame-ionization detector and a 1200×3.5-mm column (stationary phase SE-30 on Chromaton); oven temperature programming at 12 deg/min; carrier gas helium. The purity of the products was checked by TLC on Silufol UV-254 plates; the chromatograms were developed by treatment with iodine vapor.

***N*-Isopropyl-2-(2-cyclohexenyl)aniline (I).** A high-pressure reactor was charged with 1.7 g (10 mmol) of 2-(2-cyclohexenyl)aniline, 1.4 g (12 mmol) of isopropyl bromide, 10 ml of isopropyl alcohol, and 2 g of potassium carbonate, and the mixture was heated for 16 h at 100°C. The mixture was filtered, the filtrate was evaporated, the residue was dissolved in 20 ml of $CHCl_3$, the solution was washed in succession with water, a 20% aqueous solution of Na_2CO_3, and water again, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. Yield 95%, bp 126°C (3 mm). IR spectrum, ν, cm^{-1}: 3400 (NH). ^1H NMR spectrum, δ, ppm: 1.4 d (3H, CH_3, J = 6.8 Hz), 1.5 d (3H, CH_3, J = 6.8 Hz), 1.8–2.4 m (6H, $3CH_2$), 3.6 br.s (1H, NH), 3.9 m (2H, CH), 5.9 m (1H,

2'-H), 6.2 m (1H, 3'-H), 6.9–7.4 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.2 ($C^{5'}$), 22.9 and 23.2 (CH_3), 25.0 ($C^{4'}$), 28.0 ($C^{6'}$) 38.0 ($C^{1'}$), 44.0 (CH), 111.2 (C^6), 116.3 (C^4), 127.2 (C^5), 128.9 ($C^{2'}$), 129.0 (C^3), 130.3 ($C^{3'}$), 132.5 (C^2), 144.7 (C^1). Found, %: C 83.31; H 9.45; N 6.19. $C_{15}H_{21}N$. Calculated, %: C 83.67; H 9.83; N 6.50.

***N*-Benzyl-2-(2-cyclohexenyl)aniline (II).** Benzyl bromide, 1.7 g (10 mmol), was added dropwise under continuous stirring to a mixture of 5.3 g of $NaHCO_3$ and 6.9 g (40 mmol) of 2-(2-cyclohexenyl)aniline. The mixture was stirred for 24 h at room temperature, diluted with 20% aqueous sodium hydroxide, and extracted with benzene. The organic phase was separated, dried over $MgSO_4$, and evaporated. Excess initial amine was removed from the residue by vacuum distillation, and product **II** was isolated from the still residue by chromatography in a short column charged with silica gel. Yield 70%, bp 142°C (1 mm). IR spectrum, ν, cm^{-1}: 3400 (NH). ^1H NMR spectrum, δ, ppm: 1.5–2.1 m (6H, $3CH_2$), 3.4 br.s (1H, NH), 4.0 m (1H, 1'-H), 4.3 s (2H, CH_2), 5.7 m (1H, 3'-H), 5.8 m (1H, 2'-H), 6.7–7.5 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.1 ($C^{5'}$), 25.0 ($C^{4'}$), 28.1 ($C^{6'}$), 37.9 ($C^{1'}$), 48.3 (Ph**C**H_2), 110.8 (C^6), 117.1 (C^4), 125.8 (C^3), 127.4 ($C^{2'}$), 127.9 (C^5), 128.1 ($C^{3''}$, $S^{5''}$), 128.6 ($C^{4''}$), 128.7 ($C^{2''}$, $C^{6''}$), 128.8 ($C^{3'}$), 135.7 ($C^{1''}$), 139.5 (C^2), 145.3 (C^1). Found, %: C 86.24; H 7.75; N 5.02. $C_{19}H_{21}N$. Calculated, %: C 86.65; N 8.04; N 5.32.

N*-Isopropyl- and *N*-benzyl-1-iodo-1,2,3,4,4a,9a-hexahydrocarbazoles III and IV (general procedure*).** Sodium hydrogen carbonate, 10 mmol, and iodine, 2 mmol, were added to a solution of 1 mmol of amine **I** or **II** in 20 ml of carbon tetrachloride. When the initial amine disappeared, the solvent was removed by decanting, the precipitate was dissolved in 30 ml of methylene chloride, the solution was treated with 10% aqueous $Na_2S_2O_3$ (2×20 ml), and the organic phase was separated, washed with water (2×10 ml), dried over $MgSO_4$, and evaporated under reduced pressure.

Compound **III**. Yield 95%, R_f 0.6 (C_6H_6). IR spectrum, ν, cm^{-1}: 550 (C–I). ^1H NMR spectrum, δ, ppm: 1.1–2.3 m (6H, $3CH_2$), 1.3 d (3H, CH_3, J = 6.7 Hz), 1.5 d (3H, CH_3, J = 6.7 Hz), 3.2 d.t (1H, 4a-H, $J_{4a,4\text{-}ax}$ = 10.0, $J_{4a,4\text{-}eq}$ = 3.8 Hz), 3.9 d.d [1H, 9a-H, $J_{9a,1}$ = 4.4, $J_{9a,4a\text{-}eq}$ = 7.1 Hz), 4.1 t (1H, CH, J = 6.7 Hz), 4.9 d.d.d [1H, 1-H, $J_{1,2\text{-}ax}$ = 8.6, $J_{1,2\text{-}eq}$ = 4.4 Hz), 6.7–7.3 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 16.8 (C^3), 22.6, 23.1 ($2CH_3$), 30.2 (C^4), 30.5 (C^2), 35.1 (C^1), 39.4 (C^{4a}), 47.5 (CH), 68.8 (C^{9a}), 110.6 (C^8), 122.5 (C^7), 124.1 (C^5), 127.3 (C^6), 134.5 (C^{4b}), 145.2 (C^{8a}). Found, %: C 52.51; H 5.63; I 36.78; N 3.86. $C_{15}H_{20}IN$. Calculated, %: C 52.80; H 5.91; I 37.19; N 4.10.

Compound **IV**. Yield 90%. R_f 0.5 (C_6H_6). IR spectrum, ν, cm^{-1}: 550 (C–I). ^1H NMR spectrum, δ, ppm: at 20°C: 1.0–2.4 m (6H, $3CH_2$), 3.3 d.t (1H, 4a-H, $J_{4a,4\text{-}ax}$ = 11.0, $J_{4a,4\text{-}eq}$ = 6.2 Hz), 3.8 d.d [1H, 9a-H, $J_{9a,1}$ = 2.4, $J_{9a,4a\text{-}eq}$ = 6.4Hz), 4.2 d and 4.3 d (1H each, Ph**C**$\mathbf{H}_2$, J = 16.3 Hz), 4.8 d.d.d (1H, 1-H, $J_{1,2\text{-}ax}$ = 7.7, $J_{1,2\text{-}eq}$ = 2.1 Hz), 6.5 d (1H, 8-H, 7.9 Hz), 6.8 t (1H, 6-H), 7.0 t (1H, 7-H), 7.1 d (1H, 5-H, J = 7.3 Hz), 7.2–7.4 m (5H, H_{arom}); at 50°C: 1.0–2.4 m (6H, $3CH_2$), 3.4 d.t (1H, 4a-H, $J_{4a,4\text{-}ax}$ = 10.8, $J_{4a,4\text{-}eq}$ = 6.9 Hz), 3.9 d.d (1H, 9a-H, $J_{9a,1}$ = 2.7, $J_{9a,4a\text{-}eq}$ = 6.9 Hz), 4.2 d and 4.3 d (1H each, Ph**C**$\mathbf{H}_2$, J = 16.2 Hz), 4.8 d.d.d (1H, 1-H, $J_{1,2\text{-}ax}$ = 7.7, $J_{1,2\text{-}eq}$ = 2.7 Hz), 6.5 d (1H, 8-H, J = 7.9 Hz), 6.8 t (1H, 6-H), 7.0 t (1H, 7-H), 7.1 d (1H, 5-H, J = 7.3 Hz), 7.2–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9 (C^5); 29.9 (C^4); 31.1 (C^2); 31.9 (C^1); 38.3 (C^{4a}); 52.5 (CH_2); 72.2 (C^{9a}); 118.9 (C^8); 127.2 (C^7); 127.3 (C^5); 128.4 (C^6); 134.1 (C^{4b}); 138.9 (C^{8a}); 126.9, 128.5, 128.6, 138.8 (C_{arom}). Found, %: C 58.28; H 4.87; I 32.29; N 3.19. $C_{19}H_{20}IN$. Calculated, %: C 58.62; N 5.18; I 32.60; N 3.60.

(1*R,4a*R**,9a*S**)-*N*-Isopropyl-1-thiocyanato-1,2,3,4,4a,9a-hexahydrocarbazole (VII).** Potassium thiocyanate, 1 g (10 mmol), was added to a solution of 0.34 g (1 mmol) of compound **III** in 10 ml of acetonitrile. When the reaction was complete, the mixture was evaporated, and 10 ml of water and 10 ml of chloroform were added to the residue. The organic phase was separated, dried over $MgSO_4$, and evaporated under reduced pressure. Yield 0.2 g (75%). R_f 0.7 (C_6H_6). IR spectrum, ν, cm^{-1}: 2380 m (C≡N). ^1H NMR spectrum, δ, ppm: 1.2 d and 1.4 d (3H each, $2CH_3$, J = 7.0 Hz), 1.2–2.2 m (6H, $3CH_2$), 3.1 d.d.d (1H, 4a-H, J_1 = 4.0, J_2 = 8.1, J_3 = 11.5 Hz), 3.6 t (1H, 9a-H, J = 8.0 Hz), 3.7 m (1H, 1-H), 3.8 q (1H, CH, J = 7.0 Hz), 6.7 d (1H, 8-H, J = 8.3 Hz), 7.2–7.5 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.6, 21.3 ($2CH_3$); 20.9 (C^3); 24.4 (C^4); 30.5 (C^2); 43.3 (C^{4a}); 51.5 (C^1); 52.6 (CH); 63.7 (C^{9a}); 111.7 (SCN); 113.9, 121.2, 122.3, 127.4, 134.1, 150.5 (C_{arom}). Found, %: C 70.25; H 7.11; N 9.84; S 11.43. $C_{16}H_{20}N_2S$. Calculated, %: C 70.55; H 7.40; N 10.28; S 11.77.

***N*-Benzyl-1-thiocyanato-1,2,3,4,4a,9a-hexahydrocarbazole (VIII).** Potassium thiocyanate, 0.6 g (6 mmol), was added to a solution of 0.2 g (0.6 mmol) of compound **IV** in 5 ml of acetonitrile. When the reaction was complete, the solution was evaporated, and 10 ml of water and 10 ml of chloroform were added to the residue. The organic phase was separated, dried over $MgSO_4$, and evaporated under reduced

pressure. Yield 0.16 g (98%). R_f 0.4 (C_6H_6). IR spectrum, ν, cm^{-1}: 2380 m (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.5–2.2 m (6H, $3CH_2$), 3.4 m (1H, 4a-H), 3.6–3.7 m (2H, 1-H, 9a-H), 4.5 s (2H, CH_2), 6.5 d (1H, 8-H, J = 8.0 Hz), 6.8 t (1H, 6-H, J = 7.3 Hz), 7.0–7.4 m (7H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 19.0 (C^3); 27.4 (C^4); 28.3 (C^2); 39.9 (C^{4a}); 48.3 (C^1); 52.9 (CH_2); 67.7 (C^{9a}); 109.1 (C^8); 111.4 (SCN); 119.0 (C^7); 122.7 (C^5); 127.2 (C^6); 132.8 (C^{4b}); 150.8 (C^{8a}); 127.0, 127.7, 128.6, 138.4 (C_{arom}). Found, %: C 74.55; H 5.91; N 8.41; S 9.63. $C_{20}H_{20}N_2S$. Calculated, %: C 74.96; H 6.29; N 8.74; S 10.00.

(1*S,4a*R**,9a*R**)-*N*-Isopropyl-1-thiocyanato-1,2,3,4,4a,9a-hexahydrocarbazole (IX).** A mixture of 0.22 g (1 mmol) of compound **I**, 0.84 g (10 mmol) of $NaHCO_3$, 0.51 g (2 mmol) of I_2, and 0.19 g (2 mmol) of KSCN in 20 ml of acetonitrile was shaken for 24–130 h at 20°C, the progress of the reaction being monitored by TLC using benzene as eluent. When the reaction was complete, 50 ml of methylene chloride was added, the mixture was filtered, and the precipitate was washed with methylene chloride (10 ml). The organic phase was treated with a 5% aqueous solution of $Na_2S_2O_3$ (3×10 ml) and water (20 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (0.5×30 cm) using benzene as eluent. Yield 0.2 g (75%). ^{1}H NMR spectrum, δ, ppm: 1.2 d and 1.4 d (3H each, $2CH_3$, J = 7.0 Hz), 1.3–2.2 m (6H, $3CH_2$), 3.0 d.d.d (1H, 4a-H, J_1 = 4.0, J_2 = 8.1, J_3 = 11.5 Hz), 3.5 t (1H, 9a-H, J = 8.0 Hz), 3.6 m (1H, 1-H), 3.7 q (1H, CH, J = 7.0 Hz), 6.8–7.2 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.6, 20.9 ($2CH_3$); 21.2 (C^3); 24.5 (C^4); 30.1 (C^2); 42.3 (C^{4a}); 51.0 (C^1); 51.8 (CH); 65.2 (C^{9a}); 110.7 (SCN); 112.7, 127.1, 128.3, 133.2, 136.0, 152.3 (C_{arom}). Found, %: C 70.31; H 7.03; N 9.98; S 11.36. $C_{16}H_{20}N_2S$. Calculated, %: C 70.54; H 7.40; N 10.28; S 11.77.

1-Methylamino-1,2,3,4,4a,9a-hexahydrocarbazole hydroiodide (X). A 20% solution of methylamine in THF, 1 ml (7 mmol), was added to a solution of 0.2 g (0.6 mmol) of carbazole **IV** in 5 ml of acetonitrile. When the reaction was complete, the solution was evaporated, and 10 ml of water and 10 ml of chloroform were added. The organic phase was separated and dried over $MgSO_4$, and the solvent was removed to obtain 0.2 g (98%) of compound **X**. R_f 0.2 (C_6H_6). IR spectrum, ν, cm^{-1}: 3370 (NH). ^{1}H NMR spectrum, δ, ppm: 1.4–2.0 m (6H, $3CH_2$), 2.5 s (3H, NCH_3), 3.3 d.d.d (1H, 1-H, $J_{1,2\text{-}ax}$ = 3.0, $J_{1,2\text{-}eq}$ = 3.2 Hz), 3.6 d.d.d (1H, 4a-H, $J_{4a,4\text{-}ax}$ = 9.0, $J_{4a,4\text{-}eq}$ = 7.1 Hz), 3.8 d.d [1H, 9a-H, $J_{9a,1}$ = 3.5, $J_{9a,4a\text{-}eq}$ = 7.2 Hz), 4.3 d and 4.5 d (1H each, PhC**H**$_2$, J = 16.3 Hz), 6.6 d (1H, 8-H, J = 7.6 Hz), 6.8 t (1H, 6-H, J = 7.3 Hz), 7.0 m (1H, 7-H), 7.0–7.4 m (8H, H_{arom}, NH_2I). ^{13}C NMR spectrum, δ_C, ppm: 19.0 (C^3); 24.0 (C^4); 29.0 (C^2); 31.3 (NCH_3); 38.6 (C^{4a}); 53.9 (CH_2); 56.4 (C^1); 65.0 (C^{9a}); 110.4 (C^8); 119.9 (C^7); 123.0 (C^5); 127.6 (C^6); 134.7 (C^{4b}); 151.1 (C^{8a}); 127.2, 128.4, 128.6, 138.7 (C_{arom}). Found, %: C 56.84; H 5.65; I 29.78; N 6.32. $C_{20}H_{25}IN_2$. Calculated, %: C 57.14; H 6.01; I 30.19; N 6.66.

3-Allylamino-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIII). Allylamine, 0.14 g (2.4 mmol), was added with stirring to a solution of 0.6 g (2 mmol) of compound **XI** in 10 ml of acetonitrile. The mixture was left to stand for 12 h and evaporated, 10 ml of 10% aqueous sodium hydroxide and 10 ml of methylene chloride were added, and the mixture was shaken. The organic phase was separated and dried over $MgSO_4$, the solvent was removed, and the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (9:1) as eluent. Yield 0.4 g (70%). R_f 0.3. IR spectrum, ν, cm^{-1}: 3328 (NH). ^{1}H NMR spectrum, δ, ppm: 1.4–2.4 m (4H, $2CH_2$), 2.1 s (3H, CH_3), 3.0 d.t (1H, 3-H, J_1 = 3.2, J_2 = 5.3 Hz), 3.3 m (2H, CH_2), 3.9 d.t (1H, 8b-H, J_1 = 3.2, J_2 = 9.0 Hz), 3.5–4.3 br.s (2H, 2NH), 4.0 d.d (1H, 3a-H, J_1 = 3.2, J_2 = 9.0 Hz), 5.1 d.d (1H, 1'-H_A, J_1 = 1.4, J_2 = 10.2 Hz), 5.2 d.q (1H, 1'-H_B, J_1 = 1.4, J_2 = 17.1 Hz), 6.0 d.d.t (1H, 2-H, J_1 = 4.0, J_2 = 10.2, J_3 = 17.1 Hz), 6.7 t (1H, 7-H, J = 7.0 Hz), 6.9 d (1H, 6-H, J = 7.0 Hz), 7.0 d (1H, 8-H, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 30.9 (C^2), 32.0 (C^1), 46.4 (C^{8b}), 50.8 ($C^{3'}$), 67.8 (C^3), 69.2 (C^{3a}), 116.1 ($C^{1'}$), 118.3 (C^5), 118.8 (C^7), 121.8 (C^8), 128.3 (C^{8a}), 132.4 (C^6), 136.8 ($C^{3'}$), 149.0 (C^{4a}). Found, %: C 78.54; H 8.66; N 11.94. $C_{15}H_{20}N_2$. Calculated, %: C 78.90; H 8.83; N 12.27.

***N*-Allyl-3-bromo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIV).** Allyl bromide, 0.7 g (6 mmol), was added with stirring to a mixture of 0.9 g (3 mmol) of 3-iodoindole **XI** and 1.1 g (10 mmol) of $NaHCO_3$ in 20 ml of acetonitrile, and the mixture was kept for 24 h. When the reaction was complete (TLC), the solvent was distilled off under reduced pressure, and 10 ml of water and 20 ml of chloroform were added to the residue. 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 silica gel using benzene as eluent. Yield 0.4 g (39%). R_f 0.8 (C_6H_6). ^{1}H NMR spectrum, δ, ppm: 1.61–2.5 m (4H, $2CH_2$), 3.7 m (2H, CH_2), 3.9 t (1H, 8b-H, J = 8.7 Hz),

4.2 d (1H, 3a-H, J = 8.9 Hz), 4.3 m (1H, 3-H), 5.0–5.2 m (2H, CH_2), 5.8 d.d.t (1H, CH, J_1 = 5.8, J_2 = 10.2, J_3 = 17.2 Hz), 6.6 t (1H, 7-H), 6.7 d and 6.8 d (1H each, 6-H, 8-H). ^{13}C NMR spectrum, δ_C, ppm: 19.1 (CH_3), 33.1 (C^1), 33.9 (C^2), 44.4 (C^{8b}), 54.5 (CH_2), 58.4 (C^3), 79.2 (C^{3a}), 117.2 (CH_2=), 119.6 (C^7), 122.2 (C^8), 130.8 (CH=S), 134.3 (C^5), 134.8 (C^6), 149.1 (C^{4a}). Mass spectrum, *m/z:* 291 $[M]^+$, 212 $[M - Br]^+$ (base peak), 184 $[M - Br - C_2H_4]^+$, 170 $[M - Br - C_6H_6]^+$. Found, %: C 61.39; H 6.07; Br 26.89; N 4.43. $C_{15}H_{18}BrN$. Calculated, %: C 61.65; H 6.22; Br 27.34; N 4.79.

***N*-Allyl-3-amino-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XV).** Gaseous ammonia was passed over a period of 10 min through a solution of 0.6 g (2 mmol) of indole **XIV** in 10 ml of acetonitrile under stirring at 0°C. The mixture was left to stand for 0.5 h and evaporated, 10 ml of 10% aqueous sodium hydroxide and 20 ml of methylene chloride were added, and the mixture was shaken and washed with 20 ml of water. The organic phase was separated and dried over $MgSO_4$, the solvent was removed, and the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (9:1) as eluent. Yield 0.3 g (70%). R_f 0.3 (C_6H_6). IR spectrum, ν, cm^{-1}: 3370 (NH). ^{1}H NMR spectrum, δ, ppm: 1.4–1.8 m (4H, $2CH_2$), 2.3 s (3H, CH_3), 3.3 m (1H, 3-H), 3.6 d.d (1H, 3a-H, J_1 = 2.5, J_2 = 9.3 Hz), 3.8–3.9 m (5H, NCH_2, 8b-H, NH_2), 5.2 m (2H, =CH_2), 5.9 m (1H, CH=), 6.6–6.9 m (3H, 6-H, 7-H, 8-H). ^{13}C NMR spectrum, δ_C, ppm: 18.7 (CH_3), 31.5 (C^2), 32.3 (C^3), 44.0 (C^{8b}), 54.5 (NCH_2), 59.5 (C^1), 78.5 (C^{3a}), 116.2 (=CH_2), 119.3 (C^8), 119.8 (C^{8a}), 121.7 (C^6), 130.1 (C^7), 135.3 (C^5), 135.6 (CH=), 149.5 (C^{4a}). Found, %: C 78.64; H 8.65; N 12.02. $C_{15}H_{20}N_2$. Calculated, %: C 78.90; H 8.83; N 12.27.

***N*-Allyl-3-allylamino-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XVI).** Allylamine, 0.14 g (2.4 mmol), was added with stirring to a solution of 0.6 g (2 mmol) of compound **XIV** in 10 ml of acetonitrile. The mixture was left to stand for 12 h and evaporated, 10 ml of 10% aqueous sodium hydroxide and 20 ml of methylene chloride were added, the mixture was shaken, and the organic phase was separated and dried over $MgSO_4$. The solvent was removed, and the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (9:1) as eluent. Yield 0.3 g (60%). R_f 0.5 (C_6H_6). ^{1}H NMR spectrum, δ, ppm: 1.3–2.2 m (4H, $2CH_2$), 2.2 s (3H, CH_3), 3.0 m (1H, 3-H), 3.2 m (2H, CH_2), 3.6 d.d (1H, 3a-H, J_1 = 2.0, J_2 = 9.0 Hz), 3.7 m (2H, CH_2), 3.8 m (1H, 8b-H), 5.2 m (5H, $2CH_2$=, NH), 5.9 m (2H, 2CH=), 6.6 t (1H, 7-H), 6.8 d and 6.9 d (1H each, 6-H, 8-H). ^{13}C NMR spectrum, δ_C, ppm: 18.4 (CH_3), 29.7 (C^2), 31.7 (C^1), 44.1 (C^{8b}), 50.0 (NCH_2), 53.9 ($NHCH_2$), 65.3 (C^3), 75.2 (C^{3a}), 115.2 (CH_2=), 116.0 (CH_2=), 119.0 (C^8), 119.4 (C^{8a}), 121.3 (C^7), 129.7 (C^6), 135.0 (CH=), 135.1 (CH=), 136.3 (C^5), 149.2 (C^{4a}). Found, %: C 80.50; H 8.97; N 10.40. $C_{18}H_{24}H_2$. Calculated, %: C 80.50; H 9.01; N 10.44.

3-Allyl-5-iodo-7-methyl-2,2a,3,4,5,6,10b,10c-octahydro-1*H*-3,6a-diazabenzo[*a*]cyclopenta[*cd*]-azulene (XVIII). Sodium hydrogen carbonate, 10 mmol, and iodine, 2 mmol, were added to a solution of 1 mmol of compound **XVI** in 20 ml of methylene chloride. When the initial amine disappeared, the mixture was treated with a 10% aqueous solution of $Na_2S_2O_3$ (2×20 ml), and the organic phase was separated, washed with water (2×10 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure to obtain assumingly compound **XVII** which was gradually converted into **XVIII**. Yield 0.4 g (90%). R_f 0.8 (C_6H_6). ^{1}H NMR spectrum, δ, ppm: 1.7–2.6 m (4H, $2CH_2$), 2.2 s (3H, CH_3), 3.6 m (1H, 2a-H), 3.8 m (2H, 6-H), 4.0 m (2H, 1'-H), 4.2 m (1H, 10b-H), 4.35 m (1H, 10c-H), 5.1–5.3 m (2H, 4-H), 5.6 m (1H, 5-H), 5.8 m (2H, 3'-H), 6.3 m (1H, 2'-H), 6.7–6.9 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.8 (C^5), 18.4 (CH_3), 26.8 (C^1), 31.4 (C^2), 44.9 (C^{10b}), 48.1 (C^6), 54.2 ($C^{1'}$), 60.0 (C^4), 64.7 (C^{2a}), 71.7 (C^{10s}), 117.7 ($C^{3'}$), 120.7 (C^{10}), 121.1 (C^{10a}), 124.3 (C^7), 127.0 (C^9), 130.2 (C^8), 134.0 ($C^{2'}$), 148.6 (C^{6b}). Found, %: C 54.75; H 5.80; I 32.15; N 7.05. $C_{18}H_{23}IN_2$. Calculated, %: C 54.83; H 5.88; I 32.18; N 7.10.

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