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Effect of Substituents on Isomerization of *N*-Acyl-3-iodo-5-R-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]-indoles into 3,4,4a,8c-Tetrahydro-2a*H*-2-oxa-8b-azoniapentaleno[1,6-*ab*]indenes

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Abstract—Halocyclization of *ortho*-(2-cyclopenten-1-yl)aniline derivatives provided 3-halosubstituted cyclopenta[*b*]indoles. Some transformations of the latter were studied.

Keywords: cyclopenta[*b*]indoles, halogenocyclization, isomerization

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Among numerous methods of preparation of practically important compounds [1–4] the halogen-promoted procedures of alkenyl amides cyclization also find application. In some cases quaternization of the nitrogen atom occurred with the formation of pyrrolidinium halide [5, 6]; sometimes ring-chain tautomerism happened [7–9]. For such natural [10, 11] or synthetic amides [12, 13] equilibrium states are known which appear in the spectral characteristics of the compounds.

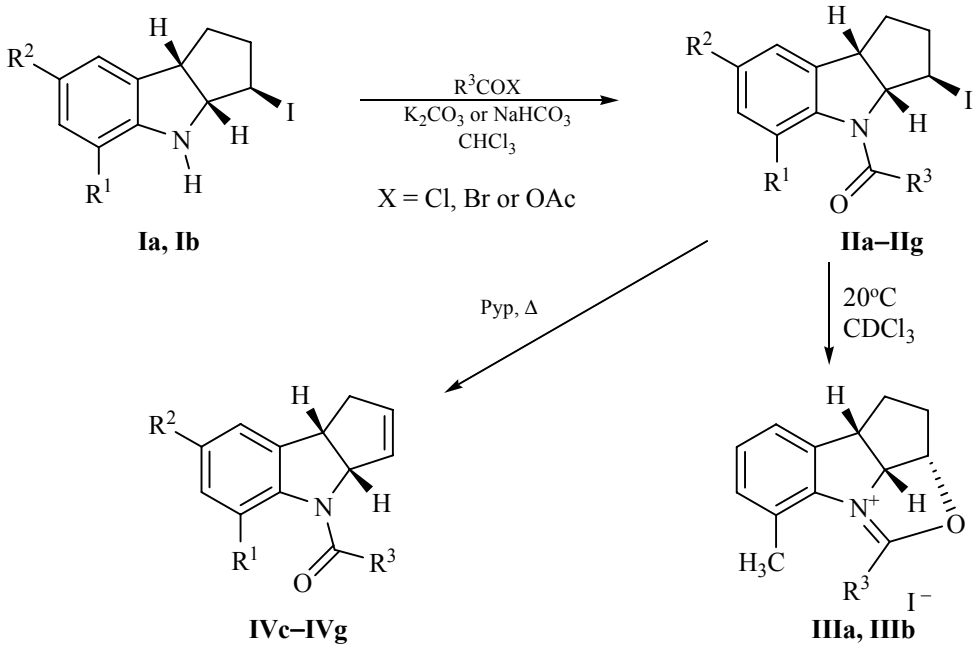
Depending on the nature the aminohalogenation products undergo further isomerization [14, 15] except for some cases, for instance, when the formed product is relatively stable [16, 17]. Iodocyclization of *ortho*-alkenylanilines is accompanied with 5-*exo*-cyclization of the products to 6-*endo*-isomers [18, 19], that did not occur in the case of *N*-tosylates, *N*-mesylates [20–23], and non-protected 3-iodo-1,2,3,3a,4,8b-hexahydro-cyclopenta[*b*]indoles [24].

Based on *N*-acetyl(benzoyl)-1-iodo-8-R-1,2,3,4,4a,9a-hexahydrocarbazoles (R = H, Me) [25] and *N*-acetyl-3-iodo-5-R-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles (R = Me, OMe) [26, 27] the process of isomerization with the formation of tetracyclic structure was investigated. The isomerization proceeded through quaternization of the nitrogen atom with a newly formed fused ring. At the same time the compounds with the other fragments at the nitrogen atom and substituents R at the aromatic ring in the cyclopenta[*b*]-indole skeleton were not studied.

In the present report the results of investigation of the effect of the substituent nature at the carbonyl carbon atom of the acyl fragment and influence of the halogen (I or Br) in the molecule of *N*-acyl-3-halogen-5-R-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole on the formation of the intramolecular cyclization products are presented.

Compounds **IIa**–**IIg** were synthesized by reaction of indolines **Ia** and **Ib** [24] with Ac_2O or AcHlg. According to the ^{1}H NMR spectra, compound **IIa** underwent spontaneous isomerization with the formation of tetracycle **IIIa**. Most characteristic region of the signals of the protons H^3, H^{3a}, H^{8b} in ^{1}H NMR spectrum of **IIa** is presented in Fig. 1; the spectra were recorded after 6, 15, and 30 days of the sample standing as a solution in $CDCl_3$. Elongation of aliphatic chain of the carboxylic acid fragment as well as its branching did not prevent the isomerization, but made it slower. In the case of compound **IIb** synthesized by similar procedure the ratio of indoline **IIb** : oxazolium iodide **IIIb** after 11 days was approximately 1 : 1 based on comparison of the

Scheme 1.



$R^1 = R^3 = CH_3$, $R^2 = H$ (**a**); $R^1 = CH_3$, $R^2 = H$, $R^3 = CH(CH_3)_2$ (**b**); $R^1 = H$, $R^2 = R^3 = CH_3$ (**c**); $R^2 = Br$, $R^2 = R^3 = CH_3$ (**d**); $R^1 = R^2 = H$, $R^3 = CH_3$ (**e**), $R^1 = CH_3$, $R^2 = H$, $R^3 = 4\text{-}NO_2C_6H_4$ (**f**); $R^1 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$ (**g**).

integral intensity of the proton signals in the ^{1}H NMR spectrum of the reaction mixture (Scheme 1).

Unlike indolines **IIa** and **IIb**, compounds **IIc** [28], **IId** [29], and **IIe** [25] did not undergo intramolecular cyclization with oxazolium iodide formation even at prolonged reflux in benzene; their reflux in piperidine easily provided tetrahydrocyclopenta[*b*]indoles **IVc** [28], **IVd** [29], and **IVe** [25]. However, an attempt to obtain cyclopenta[*b*]indole **IVa**, which is isomeric to compound **IVc**, by dehydroiodination of heterocycle **IIa** at reflux in piperidine was unsuccessful and led to the formation of complex mixture of the products.

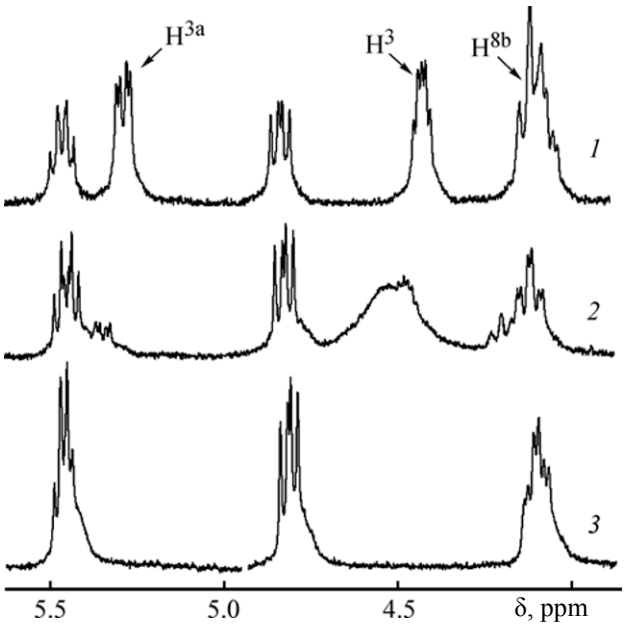


Fig. 1. Fragment of the ^{1}H NMR spectrum (the resonance region of the protons H^3, H^{3a}, and H^{8b}) of a mixture of the products **IIa** and **IIIa**; the spectra were recorded after keeping the mixture for 6 (*1*), 15 (*2*), and 30 days (*3*).

The preliminary theoretical analysis by the methods of molecular mechanics showed that isomers **IIc** and **IId** are more stable compared to **IIa** and **IIb** approximately by 4–6 kcal mol^{-1}. *N*-Aroyl derivatives **IIg** and **IIh** despite the presence of a substituent in the ortho-position of the aromatic ring and a sufficiently high calculated value of their formation energy occurred to be stable against isomerization (Table 1). The lengths of the amide and C=O bonds in the compounds are close (Table 1).

The obtained calculation data did not allow unambiguous conclusion on the decisive impact of the energy factors on the probability of intramolecular cyclization. Thus, in the case of *N*-acetyl- and *N*-isobutyryl derivatives **IIa** and **IIb** the isomerization was most probably caused by different spatial orientation of the oxygen atoms of the carbamide group compared to their analogs **IIc** and **IId**. The

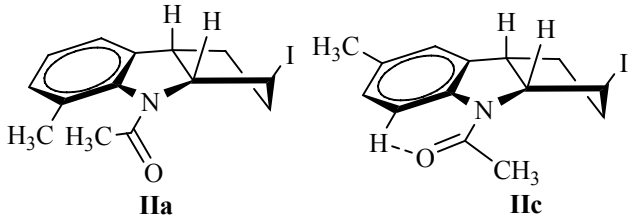
formation of the product of intramolecular cyclization from aroyl derivatives **IIg** and **IIh** was prevented by different nature of the carboxylic acid residue. X-Ray diffraction data for the epoxidation product of indoline **IVc** allowed to regard the interaction between the hydrogen atom at the aromatic ring and the oxygen atom of the carboxylic acid moiety (here $C^5H\cdots O$) as a weak intramolecular hydrogen bond [28].

With a high probability we may assume the existence of a similar weak intramolecular hydrogen bond between the oxygen atom and aromatic proton H^5 located close to it in **IIc**. This may be a factor ensuring the location of the oxygen atom in the plane opposite to the C^3 atom. Concerning compound **IIa** the steric factor of the *ortho*-methyl group most probably excluded mutual location of the atoms in the same plane (Scheme 2).

Comparison of the NMR spectra of compounds **IIa** and **IIc** showed some distinctions, which are most probably connected with different location of the acetyl group. In the ^{1}H NMR spectra of **IIa** (Fig. 1a) and **IIc** (Fig. 2) the signals of the protons H^{3a} had similar spin-spin coupling constants, 8.1 and 8.3 Hz, respectively. Moreover, the signal of the proton H^{3a} in **IIa** resonated as a doublet of doublets with a small constant (3.1 Hz), while the signal of the same proton in **IIc** was present as a doublet. Multiplicity of the signals of the protons H^3 in both isomeric iodides **IIa** and **IIc** was also different. Thus, in the ^{1}H NMR spectrum of compound **IIa** the signal of the proton H^3 was present as a doublet of triplets at 4.25 ppm (Fig. 1a), whereas in the spectrum of **IIc** the signal was a doublet (Fig. 2).

Under reflux in piperidine compounds **IIg** and **IIh** undergo dehydrohalogenation to form heterocycles **IVg** and **IVh.** After the workup of the reaction mixture and removing excess piperidine the residue contained only indolines **IVg, IVh** that indicated stability of the starting iodides to the heat-induced intramolecular isomerization.

Scheme 2.



IIa **IIc**

Calculated values of bond lengths and energy of formation for compounds **IIa**–**IId**, **IIg**, and **VIa**

Comp. no.	*d*, Å		Energy of formation, kcal mol^{-1}
	C(O)–N	C=O	
IIa	1.35	1.21	11.7
IIb	1.39	1.22	14.9
IIc	1.37	1.19	7.9
IId	1.37	1.23	8.7
IIg	1.38	1.23	11.3
VIa	1.38	1.22	14.4

Aiming to reveal the effect of the halogen at C^3 atom on the possibility of isomerization to form oxazole structures, 3-bromo substituted cyclopenta[*b*]-indoles **VIa** [29] and **VIb** were prepared from amides **Va** and **Vb** [13]. According to literature data the energy, length, and polarity of the bonds C–I and C–Br in haloalkanes differ approximately by 10%. Yet the difference in the values of polarizability of the bonds C–Br ($\alpha = 9.6 \times 10^{-24}$ cm^3) and C–I ($\alpha = 14.6 \times 10^{-24}$ cm^3) reaches $\Delta\alpha = 5 \times 10^{-24}$ cm^3.

According to the NMR data, after maintaining the solution of compound **VIa** in $CDCl_3$ for 48 h the ^{1}H NMR spectrum contained the signals of the tetracyclic product **VII** at 5.33 and 4.73 ppm. Probably, the change of iodine for bromine slowed down the process of intramolecular secondary cyclization. The ratio of the integral intensities of the signals in the ^{1}H NMR spectrum of a mixture of compounds **VIa** and **VII** after 10 days was ~ 4 : 1 (Scheme 3).

Compound **VIb** did not undergo isomerization at all: Its reflux in piperidine caused formation of indoline **IVc** in good yield.

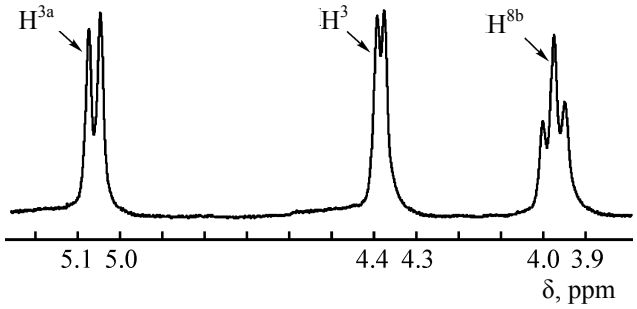
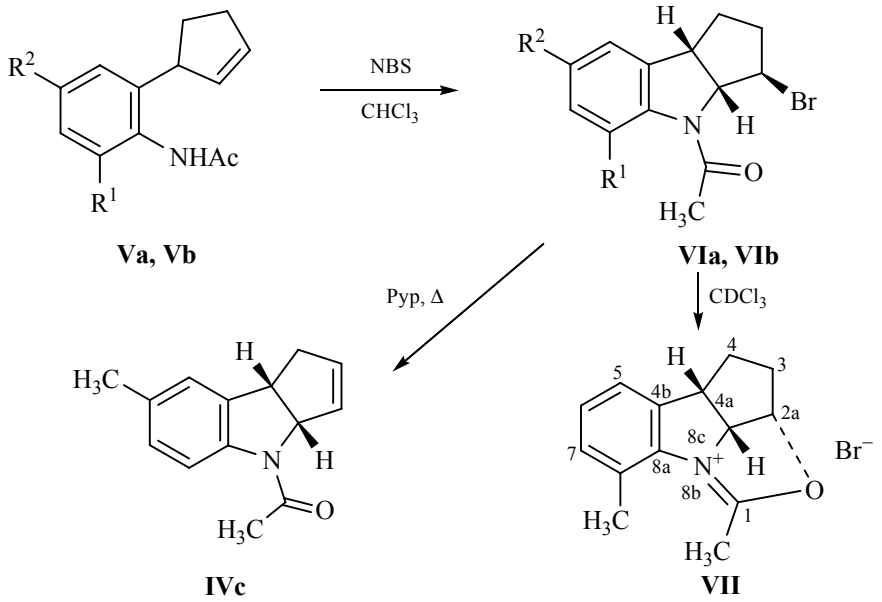


Fig. 2. Fragment of the ^{1}H NMR spectrum of compound **IIc**.

Scheme 3.



$R^1 = CH_3$, $R^2 = H$ (**a**), $R^1 = H$, $R^2 = CH_3$ (**b**).

The mass spectrum of **VIb** contained the molecular ion with *m*/*z* 293.0406. In the ^{13}C NMR spectrum of the compound the signal of bromine-substituted C^3 atom resonated at 56 ppm that was in accordance with the literature data.

The bromine atom at C^3 in compound **VIb** had almost no impact on splitting character of the proton signals. The NMR spectra of **IIc** and **VIb** are similar: the proton H^{3a} in the spectrum of compound **IIc** resonated as a doublet at 5.08 ppm (*J* 8.2 Hz), and in **VIb** the same proton was present as a doublet at 4.96 ppm (*J* 7.7 Hz). The calculated bond lengths occurred to be close to standard values. Thus, the C–Br bond length in compound **VIa** was 1.95 Å, and the C–I bond length in compound **IIa** was 2.16 Å.

In summary, *N*-acetyl-3-iodo-, -3-bromo-, and *N*-isobutyryl-3-iodo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles underwent isomerization with the formation of the corresponding 3,4,4a,8c-tetrahydro-2a*H*-2-oxa-8b-azoniapentaleno[1,6-*ab*]indenes. Similar compounds containing no methyl substituent in the *ortho*-position did not undergo the isomerization. For the compounds with benzoyl group at the nitrogen atom the discussed isomerization is impossible.

EXPERIMENTAL

IR spectra were recorded on an IR Presstige-21 (Shimadzu) Fourier spectrophotometer. ^1H and ^{13}C NMR spectra of the solutions in $CDCl_3$ were registered on a Bruker Avance III 500 spectrometer operating at 500.13 and 125.73 MHz, respectively, internal reference TMS. Mass spectra were obtained on a ThermoFinnigan MAT 95 XP and LCMS-2010EV (APCI) instruments (mobile phase – acetonitrile–water, 95 : 5). Elemental analysis was performed on a CHNS Elemental Analyzer EURO EA-3000 instrument. Column chromatography was performed using silica gel MN Kieselgel 60 (40–100 μm). TLC analysis was done on Sorbfil plates (Sorbpolimer, Krasnodar), developing with iodine vapor. Computations were carried out with the use of HyperChem 8.0 software [30].

(3*R,3a*R**,8b*S**)-3-Iodo-4-acetyl-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (IIa)**. To a solution of 1.495 g (5 mmol) of cyclopenta[*b*]-indole **Ia** in 2 mL of chloroform was added with stirring 1.5 g (14.7 mmol) of acetanhydride. The reaction mixture was kept for 4 h at 20°C, after that 4 g (48.8 mmol) of $NaHCO_3$ and 25 mL of water were added. The reaction mixture was stirred until evolution of CO_2 ceased. The product was extracted with chloroform (130 mL), the organic layer was dried over $MgSO_4$, and the solvent was evaporated in a vacuum. The residue was purified by column chromatography eluting with benzene. Yield 1.125 g (66%), oily liquid, R_f 0.2 (benzene). ^1H NMR spectrum, δ, ppm: 1.63–1.79 m (1H, H^{1A}), 1.92–2.13 m (2H, H^{1B}, H^{2A}), 2.23 s

(3H, $ArCH_3$), 2.38 s [3H, $C(O)CH_3$], 2.42–2.58 m (1H, H^{2B}), 3.97 t (1H, H^{8b}, *J* 8.1 Hz), 4.27 m (1H, H^3), 5.04 d.d (1H, H^{3a}, *J* 3.1, *J* 8.1 Hz), 6.80–7.05 m ($3H_{Ar}$). ^{13}C NMR spectrum, δ_C, ppm: 20.97 and 23.91 (CH_3), 31.31 (C^3), 31.79 and 36.82 (C^1, C^2), 45.60 (C^{8b}), 76.25 (C^{3a}), 121.19, 125.80, 130.42 (C^6, C^7, C^8), 128.59, 136.38, 140.66 (C^{4a}, C^5, C^{8a}), 169.60 (C=O). Mass spectrum (APCI, 70 eV), *m*/*z* (I_{rel}, %): 342 (100) $[M + H]^+$, 83 (100) $[M + CH_3CN]^+$. Found, %: C 49.17; H 4.66; I 37.02; N 3.99. $C_{14}H_{16}INO$. Calculated, %: C 49.28; H 4.73; I 37.19; N 4.11.

(3*R,3a*R**,8b*S**)-3-Iodo-4-isobutyryl-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (IIb)**. To a solution of 0.299 g (1 mmol) of cyclopenta[*b*]-indole **Ia** in 2 mL of chloroform was added with stirring 0.213 g (2 mmol) of isobutyric acid chloride in 3 mL of $CHCl_3$ followed by addition of 0.207 g (1.5 mmol) of K_2CO_3. Next, 5 mL of water was added, and the mixture was stirred for 30 min. The product was extracted with chloroform; the organic layer was dried over $MgSO_4$ and concentrated in a vacuum. The residue was purified by column chromatography eluting with benzene. Yield 0.245 g (66%), colorless oil, R_f 0.3 (benzene). ^1H NMR spectrum δ, ppm: 1.25 d (3H, CH_3, *J* 6.6 Hz), 1.38 d (6H, CH_3, *J* 6.6 Hz), 1.54–1.67 m (1H, H^{1A}), 1.83–2.05 m (2H, H^{1B}, H^{2A}), 2.15 s (3H, $ArCH_3$), 2.46–2.59 m (1H, H^{2B}), 3.11 quintet (1H, CH, *J* 6.6 Hz), 3.95 t (1H, H^{8b}, *J* 8.0 Hz), 4.22–4.30 m (1H, H^3), 5.14 d.d (1H, H^{3a}, *J* 2.6, *J* 8.0 Hz), 6.80–7.05 m ($3H_{Ar}$). Found, %: C 51.93; H 5.37; I 34.19; N 3.72. $C_{16}H_{20}INO$. Calculated, %: C 52.04; H 5.46; I 34.37; N 3.79.

(3*R,3a*R**,8b*S**)-3-Iodo-4-(4-nitrobenzoyl)-5-methyl-1,2,3,3a,4,8b-hexaydrocyclopenta[*b*]indole (IIf)** was prepared similarly from 0.3 g (1 mmol) of cyclopenta[*b*]indole **Ia** and 0.223 g (1.2 mmol) of 4-nitrobenzoyl chloride in the presence of 0.276 g (2 mmol) of K_2CO_3. Yield 0.376 g (86%), R_f 0.23 (benzene). ^1H NMR spectrum, δ, ppm: 1.53–1.67 m (1H, H^{1A}), 2.06–2.19 m (2H, H^{1B}, H^{2A}), 2.13 s (3H, CH_3), 2.38–2.51 m (1H, H^{2B}), 4.00 t (1H, H^{8b}, *J* 6.9 Hz), 4.50 d (1H, H^3, *J* 6.2 Hz), 4.85 d.d (1H, H^{3a}, *J* 0.7, *J* 6.9 Hz), 7.06–7.17 m ($3H_{Ar}$), 7.84 d (2H, $H^{2',6'}$, *J* 8.0 Hz), 8.36 d (2H, $H^{3',5'}$, *J* 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.00 (CH_3), 31.41 (C^1), 32.55 (C^3), 37.40 (C^2), 46.90 (C^{8b}), 77.52 (C^{3a}), 121.26, 123.90, 126.68, 128.27, 129.74, 130.25 (C^6, C^7, C^8, $C^{2',6'}$, $C^{3',5'}$), 128.66, 136.00, 140.85, 141.27, 149.24 (C^{4a}, C^5, C^{8a}, $C^{1'}$, $C^{4'}$), 168.63 (NC=O). Found, %: C 50.80; H 3.73; I 28.14; N 6.15. $C_{19}H_{17}IN_2O_3$. Calculated, %: C 50.91; H 3.82; I 28.31; N 6.25.

(3*R,3a*R**,8b*S**)-4-Benzoyl-3-iodo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (IIg)** was prepared similarly from 0.598 g (2 mmol) of indoline **Ib** and 0.323 g (2.3 mmol) of benzoyl chloride in the presence of 0.414 g (3 mmol) of K_2CO_3. Yield 0.708 g (87%), R_f 0.35 (benzene). ^1H NMR spectrum, δ, ppm: 1.51–1.64 m (1H, H^{1A}), 1.82–2.08 m (2H, C^2H_2), 2.13 s (3H, CH_3), 2.38–2.51 m (1H, H^{1B}), 3.97 t (1H, H^{8b}, *J* 6.8 Hz), 4.56 d (1H, H^3, *J* 5.3 Hz), 4.93 d (1H, H^{3a}, *J* 6.8 Hz), 7.02–7.70 m ($8H_{Ar}$). Found, %: C 56.48; H 4.42; I 31.31; N 3.38. $C_{19}H_{18}INO$. Calculated, %: C 56.59; H 4.50; I 31.47; N 3.47.

(2a*R,4a*R**,8c*S**)-1,8-Dimethyl-2,4,4a,8c-tetrahydro-3*H*-2-oxa-8b-azoniapentaleno[1,6-*ab*]indene iodide (IIIa)**. A solution of 0.3 g of compound **IIa** in 5 mL of petroleum ether was stirred for 30 days at room temperature. The product was precipitated with benzene; the crystalline precipitate was filtered off, washed three times with benzene, and dried in air. Yield 0.1 g, pale grey amorphous powder. ^1H NMR spectrum, δ, ppm: 1.79–1.93 m (2H, CH_2), 1.95–2.13 m (1H, H^{3A}), 2.02 s (3H, CH_3), 2.20–2.35 m (1H, H^{3B}), 2.64 s (3H, CH_3), 4.11 d.t (1H, H^{4a}, *J* 4.5, 8.8 Hz), 4.96 d.d (1H, H^{8c}, *J* 6.0, 8.8 Hz), 5.46 q (1H, H^{2A}, *J* 6.0 Hz), 7.13 d (1H, H_{Ar}, *J* 7.7 Hz), 7.16 d (1H, H_{Ar}, *J* 7.7 Hz), 7.27 t (1H, H_{Ar}, *J* 7.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.84 and 21.87 ($2CH_3$), 29.33 and 30.53 (C^3, C^4), 45.87 (C^{4a}), 63.21 (C^{2a}), 74.15 (C^{8c}), 122.32, 128.64, 129.93 (C^5, C^6, C^7), 127.74, 137.06, 137.89 (C^8, C^{8a}, C^{4b}), 170.16 (C^1). Found, %: C 49.22; H 4.69; I 36.98; N 3.97. $C_{14}H_{16}INO$. Calculated, %: C 49.28; H 4.73; I 37.19; N 4.11.

(2a*R,4a*R**,8c*S**)-1-Isobutyryl-8-methyl-2,4,4a,8c-tetrahydro-3*H*-2-oxa-8b-azoniapentaleno[1,6-*ab*]-indene iodide (IIIb)** was prepared similarly but in a solvent-free conditions. Yield 0.4 g, grey powder, mp 194–196°C. ^1H NMR spectrum, δ, ppm: 0.82 d (3H, CH_3, *J* 7.0 Hz), 0.90 d (3H, CH_3, *J* 7.0 Hz), 1.80–2.14 m (4H, $2CH_2$), 2.44 quintet (1H, CH, *J* 7.0 Hz), 2.45 s (3H, CH_3), 4.00 d.t (1H, H^{4a}, *J* 2.5, 8.4 Hz), 4.77 d.d (1H, H^{8c}, *J* 6.9, 8.4 Hz), 5.32 d.q (1H, H^{2A}, *J* 2.6, 6.0 Hz), 7.13–7.35 m ($3H_{Ar}$). ^{13}C NMR spectrum, δ_C, ppm: 18.07, 18.18, 18.99 (CH_3), 28.94, 30.92 (C^3, C^4), 34.24 (CH), 45.42 (C^{4a}), 63.51 (C^{2a}), 74.12 (C^{8c}), 122.24, 129.67, 130.14 (C^5, C^6, C^7), 129.01, 134.76, 139.46 (C^8, C^{8a}, C^{4b}), 175.59 (C^1). Found, %: C 51.91; H 5.39; I 34.15; N 3.70. $C_{16}H_{20}INO$. Calculated, %: C 52.04; H 5.46; I 34.37; N 3.79.

(3a*R,8b*R**)-4-Acetyl-7-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (IVc)**. A solution of 0.175 g

(0.59 mmol) of compound **VIb** in 3 mL of piperidine was refluxed for 5 h followed by evaporation in a vacuum. The residue was dissolved in 50 mL of chloroform, and washed with saturated solution of $NaHCO_3$. The organic layer was separated, dried over $MgSO_4$, and concentrated in a vacuum. The residue was purified by chromatography. Yield 0.095 g (75%). The physicochemical characteristics of the prepared compound were identical to those described earlier [12, 28].

(3a*R,8b*R**)-5-Methyl-4-(4-nitrobenzoyl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (IVf)** was prepared similarly from 0.124 g (0.28 mmol) of compound **IIf**. Yield 0.064 g (72%), R_f 0.25 (benzene), mp 161–163°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, CH_3), 2.63 d (1H, H^{1A}, *J* 17.0 Hz), 2.85 d.d (1H, H^{1B}, *J* 7.2, 17.0 Hz), 4.05 t (1H, H^{8b}, *J* 7.2 Hz), 5.20 br. s (1H, H^{3a}), 5.86–5.97 m (2H, HC=CH), 7.07–7.14 m ($2H_{Ar}$), 7.34–7.36 m ($1H_{Ar}$), 7.91 d ($2H_{Ar}$, *J* 7.9 Hz), 8.34 d ($2H_{Ar}$, *J* 7.9 Hz). Found, %: C 71.08; H 4.91; N 8.61. $C_{19}H_{17}IN_2O_3$. Calculated, %: C 71.24; H 5.03; N 8.74.

(3a*R,8b*R**)-4-Benzoyl-5-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (IVg)** was prepared similarly from 0.188 g (0.47 mmol) of compound **IIg**. Yield 0.084 g (65%), R_f 0.1 (benzene). ^{1}H NMR spectrum, δ, ppm: 2.19 s (3H, CH_3), 2.62 d.d (1H, H^{1A}, *J* 2.2, 17.6 Hz), 2.82 d.d.q (1H, H^{1B}, *J* 2.0, 10.2, 17.6 Hz), 4.00 t (1H, H^{8b}, *J* 7.0 Hz), 5.23 m (1H, H^{3a}), 5.84–5.96 m (2H, HC=CH), 7.06–7.10 m ($3H_{Ar}$), 7.46–7.52 m ($3H_{Ar}$), 7.76 d.d ($2H_{Ar}$, *J* 2.5, 8.0 Hz). Found, %: C 82.76; H 6.13; N 4.98. $C_{19}H_{17}NO$. Calculated, %: C 82.88; H 6.22; N 5.09.

(3*R,3a*R**,8b*S**)-*N*-Acetyl-3-bromo-5-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (VIa)**. A mixture of 0.43 g (2 mmol) of compound **Va** and 0.361 g (2.04 mmol) of *N*-bromosuccinimide in 10 mL of anhydrous chloroform was stirred for 24 h at room temperature. The reaction progress was monitored by TLC eluting with benzene. After removing the solvent the residue was purified by chromatography eluting with benzene. Yield 0.39 g (66%), R_f 0.12 (benzene). ^{1}H NMR spectrum, δ, ppm: 1.71–1.84 m, 1.92–2.09 m, 2.44–2.54 m (4H, $2CH_2$), 2.23 s (3H, $2CH_3$), 2.39 s (3H, $2CH_3$), 4.06 t (1H, H^{8b}, *J* 7.7 Hz), 4.28 quintet (1H, H^3, *J* 2.6 Hz), 4.93 d.d (1H, H^{3a}, *J* 2.6, 7.7 Hz), 6.97–7.06 m ($3H_{Ar}$). ^{13}C NMR spectrum, δ_C, ppm: 20.83 and 23.80 ($2CH_3$), 30.78 and 34.82 (C^1, C^2), 45.28 (C^{8b}), 55.37 (C^3), 74.67 (C^{3a}), 120.98, 125.59, 130.24 (C^6, C^7, C^8), 135.87, 136.11, 138.30 (C^5, C^{4a}, C^{8a}), 169.57 (C=O). Found, %: C 57.07; H 5.40; Br 27.07; N 4.67. $C_{14}H_{16}BrNO$. Calculated, %: C 57.16; H 5.48; Br 27.16; N 4.76. Compound **VIa** at storage converts to compound **VII**.

(3*R,3a*R**,8b*S**)-*N*-Acetyl-3-bromo-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (VIb)** was prepared similarly from 1.28 g (6 mmol) of anilide **Vb** and 1.08 g (6.6 mmol) of *N*-bromosuccinimide. Yield 1.23 g (69%), pale grey powder, mp 122–123°C (EtOH). IR spectrum, ν, cm^{-1}: 1653 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.00–2.70 m (4H, $2CH_2$), 2.31 s (3H, $ArCH_3$), 2.35 s [3H, $C(O)CH_3$], 4.05 t (1H, H^{8b}, *J* 7.7 Hz), 4.37 d (1H, H^3, *J* 4.6 Hz), 4.96 d (1H, H^{3a}, *J* 7.7 Hz), 6.98 s (H^8), 7.00 d ($1H_{Ar}$, *J* 7.9 Hz), 7.99 d ($1H_{Ar}$, *J* 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.90 and 23.93 (CH_3), 31.69 and 34.11 (C^1, C^2), 44.93 (C^{8b}), 56.94 (C^3), 74.35 (C^{3a}); 116.17, 124.46, 128.48 (C^7, C^5, C^8); 133.21, 133.96, 140.34 (C^6, C^{8a}, C^{4a}), 168.77 (C=O). Mass spectrum: *m*/*z* 293.0406 $[M]^+$ (calculated for $C_{14}H_{16}BrNO$: 293.0406). Found, %: C 57.09; H 5.42; Br 27.11; N 4.68. $C_{14}H_{16}BrNO$. Calculated, %: C 57.16; H 5.48; Br 27.16; N 4.76.

(2a*R,4a*R**,8c*S**)-1,8-Dimethyl-3,4,4a,8c-tetrahydro-2a*H*-2-oxa-8b-azoniapentaleno[1,6-*ab*]indene bromide (VII)**. A solution of 0.13 g of compound **VIa** in 2 mL of benzene was kept at room temperature for 60 days. The formed colorless needle-like crystals were filtered off and dried. Yield 0.035 g, mp 169–172°C (benzene). ^{1}H NMR spectrum, δ, ppm: 1.71–2.54 m (4H, $2CH_2$), 2.03 s (3H, CH_3), 2.48 s (3H, CH_3), 3.91 d.t (1H, H^{4a}, *J* 1.8, 9.0 Hz), 4.56 d.d (1H, H^{8c}, *J* 6.0, 9.0 Hz), 5.16 d.q (1H, H^{2a}, *J* 1.5, *J* 6.0 Hz), 6.98–7.18 m ($3H_{Ar}$). ^{13}C NMR spectrum, δ_C, ppm: 18.41 and 21.46 (CH_3), 29.04 and 30.79 (C^3, C^4), 45.79 (C^{4a}), 63.07 (C^{2A}), 73.50 (C^{8c}), 122.06, 129.40, 129.79 (C^5, C^6, C^7), 135.87, 136.11, 138.30 (C^8, C^{8a}, C^{4b}), 169.90 (C^1). Found, %: C 57.06; H 5.39; Br 27.04; N 4.62. $C_{14}H_{16}BrNO$. Calculated, %: C 57.16; H 5.48; Br 27.16; N 4.76.

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