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Reactions of *N*- and *C*-Alkenylanilines: VIII.* Synthesis of Functionalized Cycloalka[*b*]indoles from *o*-(Cycloalk-2-en-1-yl)anilines

R. R. Gataullin[a], N. A. Likhacheva[a], K. Yu. Suponitskii[b], and I. B. Abdrakhmanov[a]

[a] *Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia*
e-mail: chemorg@anrb.ru

[b] *Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, Moscow, Russia*

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Abstract—*N*-Acyl-2-(cyclohex-2-en-1-yl)anilines react with molecular iodine to give the corresponding *N*-acyl-1-iodo-1,2,3,4,4a,9a-hexahydrocarbazoles which undergo isomerization into 1-R-2a,3,4,5,5a,10a-hexahydro[1,3]oxazolo[5,4,3-*j*,*k*]carbazol-10-ium iodides; no isomerization occurs with *N*-acetyl-3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole. The reaction of *N*-*p*-tolylsulfonyl-3,4,4a,9a-tetrahydrocarbazoles with hydrogen peroxide leads to the formation of a single 1,2-epoxy derivative with *trans* orientation of the nitrogen- and oxygen-containing rings. *N*-*p*-Tolylsulfonyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles give rise to the corresponding 2,3-epoxy derivatives with both *trans* and *cis* orientation of the dihydropyrrole and oxirane fragments. The resulting epoxides undergo *trans*-opening with formation of *N*-*p*-tolylsulfonyl-1-hydroxy-2-methoxy-1,2,3,4,4a,9a-hexahydrocarbazoles and *N*-*p*-tolylsulfonyl-3-hydroxy-2-methoxy-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles on heating in methanol in the presence of KU-2 cation exchanger. Mutual orientation of the oxirane and nitrogen-containing rings in the epoxides derived from cyclopenta[*b*]-indoles was proved by X-ray analysis.

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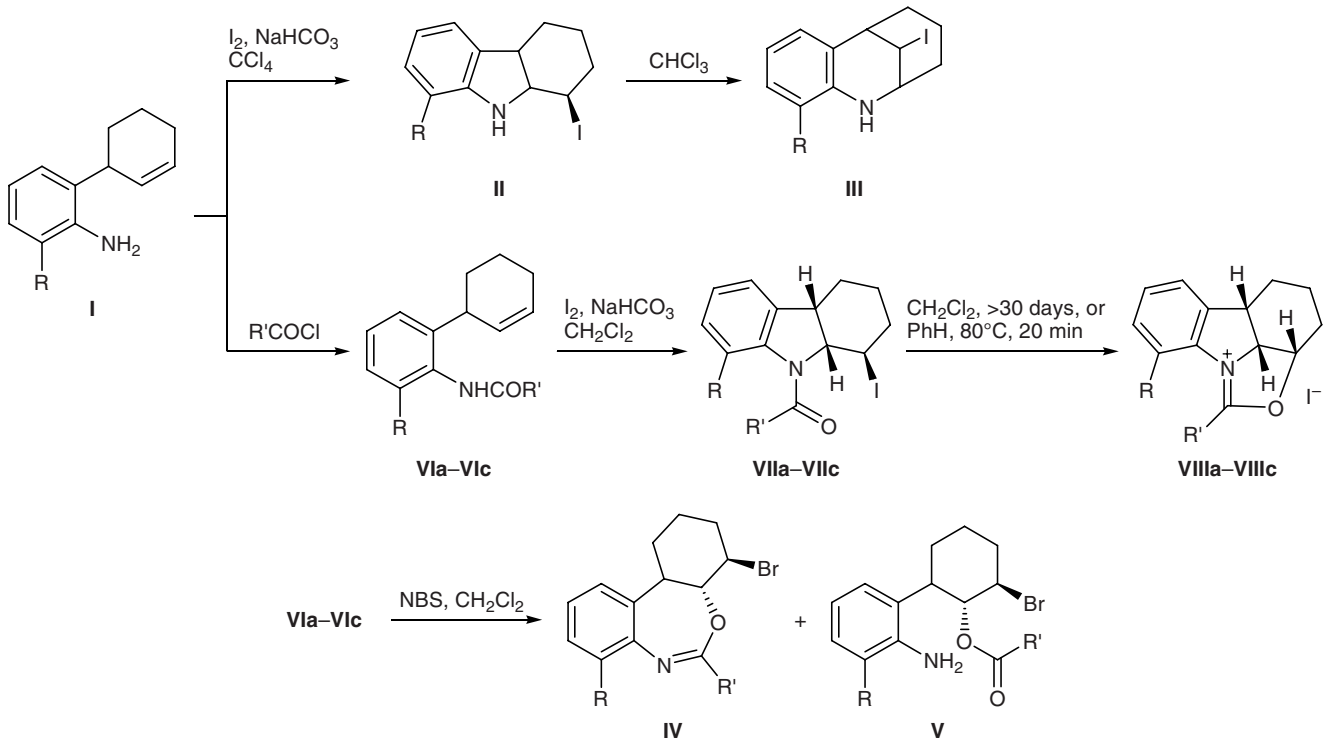
Compounds of the cycloalka[*b*]indole series exhibit antitumor [2] and antidepressant [3] activity and are used in the synthesis of biologically active substances [4–6]; cycloalka[*b*]indole fragment is the base structure of numerous natural alkaloids. Therefore, development of new methods for their preparation attracts attention of many researchers [7–16]. However, the number of publications on the synthesis of difunctional derivatives of these compounds remains so far insignificant.

In the present article we report on the results of our study on the development of procedures for the synthesis of some 1,2-functionalized hexahydrocarbazoles and 2,3-disubstituted perhydrocyclopenta[*b*]indoles from readily accessible *o*-(cycloalk-2-en-1-yl)anilines. The key step in the construction of their tricyclic skeleton is halocyclization of cycloalkenylanilines, which was extensively studied by us previously. We found that not all cycloalka[*b*]indoles available through the above reaction can be used for the synthesis of difunctional derivatives. As we showed in [17], 1-halohexahydrocarbazoles **II** having no protecting group on the nitrogen atom undergo isomerization into 3-iodotetrahydroquinolines **III** (Scheme 1). Hexahydrocarbazoles **VIIa** [18], **VIIb** [17], and **VIIc** obtained by iodocyclization of *N*-acyl-2-(cyclohex-2-en-1-yl)anilines **VIa**–**VIc** turned out to be involved in subsequent isomerization in solution on prolonged storage or on heating for a short time to give fused tetracyclic compounds **VIIIa** [18], **VIIIb**, and **VIIIc**.

Anilides **VIa**–**VIc** showed a dependence of the structure of the bromination product on the nature of the halogenating agent: molecular bromine gave rise exclusively to (dibromocyclohexyl)anilides [18], while reactions of anilides **VIa**–**VIc** with *N*-bromosuccinimide afforded 7-exocyclization products **IV** [18] which were partially hydrolyzed to amines **V** during work-up. Hexahydrocyclopenta[*b*]indole **X** obtained by acetylation of compound **IX** [19] underwent isomerization into tetrahydrocyclopenta[*b*]indole **XI** in

* For communication VII, see [1].

Scheme 1.



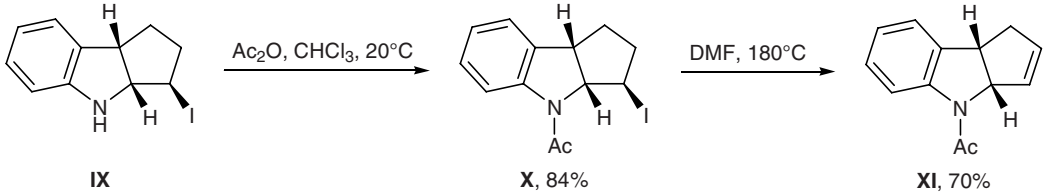
R′ = Ph, R = H (**a**), Me (**c**); R′ = Me, R = H (**b**).

a good yield on heating in dimethylformamide at 180°C (Scheme 2).

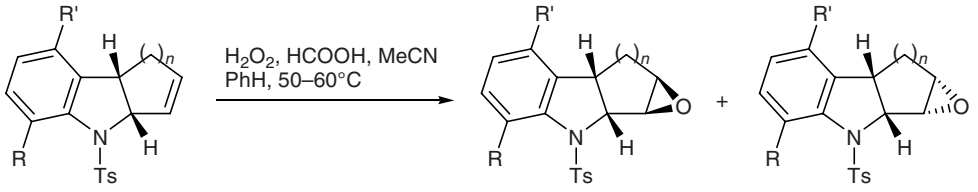
The most convenient starting compounds for the synthesis of cycloalka[*b*]indoles were *N*-methylsulfonyl [20] or *N*-*p*-tolylsulfonyl derivatives of *o*-cycloalkenylanilines [21], which did not undergo isomerization. By heating 1-halo-*N*-*p*-tolylsulfonyl-1,2,3,4,-4a,9a-hexahydrocarbazoles or 3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles in piperidine we obtained the corresponding tetrahydrocycloalka[*b*]indoles **XIIa**–**XIIf** [21] (Scheme 3). Oxidation of the latter with hydrogen peroxide in the presence of formic acid in an acetonitrile–benzene mixture at 50–60°C gave stereoisomeric epoxy derivatives **XIIIa**–**XIIIf** and **XIVd**–**XIVf**. We previously found [20] that oxidation of an *N*-methylsulfonyl analog of **XIId** with dimethyldioxirane gives 95% of the corresponding epoxide with *trans* orientation of the nitrogen-containing and oxirane rings (an analog of **XIIId**). In the reactions with H_2O_2, the ratio of **XIIId**–**XIIIf** and **XIVd**–**XIVf** was about 1:1, presumably due to smaller size of the oxidant molecule. The reaction mixtures also contained unchanged initial compounds **XIId**–**XIIf**. Compounds **XIIIe**, **XIIIf**, **XIVe**, and **XIVf** were isolated as individual substances. In the oxidation of **XIId**, only epoxide **XIVd** was isolated (its R_f value was smaller than that of isomer **XIIId**). We failed to separate isomer **XIIId** from initial compound **XIId** and *cis* isomer **XIVd**.

The structure of the isolated epoxy derivatives was determined on the basis of their spectral parameters. Mutual orientation of the oxirane and dihydropyrrole rings in these compounds was proved by X-ray analysis of single crystals of **XIIIf** and **XIVf** as examples

Scheme 2.



Scheme 3.



XIIa–XIIf **XIIIa–XIIIf** **XIVd–XIVf**

n = 2, R = Me, R′ = H (**a**), R = MeO, R′ = H (**b**), R = R′ = Me (**c**); *n* = 1, R = Me, R′ = H (**d**), R = MeO, R′ = H (**e**), R = R′ = Me (**f**).

(Fig. 1). The five-membered rings in *trans* isomer **XIIIf** are fairly flat; the mean-square deviations of atoms from the planar structures are 0.055 and 0.031 Å, respectively, for the $N^4C^{4a}C^{8a}C^{8b}C^{3a}$ and $C^1C^2C^3C^{3a}C^{8b}$ rings. In the molecule of *cis* isomer **XIVf**, analogous rings are less planar: the mean-square deviations are 0.092 and 0.088 Å, respectively, for the $N^4C^{4a}C^{8a}C^{8b}C^{3a}$ and $C^1C^2C^3C^{3a}C^{8b}$ rings. The dihedral angles between the $C^1C^2C^3C^{3a}C^{8b}$ ring, on the one hand, and $N^4C^{4a}C^{8a}C^{8b}C^{3a}$ and $C^2C^3O^1$, on the other, are 65.57(8) and 74.12(10)° for the *trans* isomer and 67.73(7) and 79.86(10)° for the *cis* isomer, respectively; it is seen that these angles in both isomers are fairly similar. The configuration of the *p*-tolylsulfonyl group was described by the torsional angles $C^{4a}N^4S^1O^2$, $C^{3a}N^4S^1O^3$, and $O^2S^1C^{11}C^{12}$ which were equal to 53.7, 54.3, and 43.6°, respectively, for isomer **XIIIf** and to –48.1, 62.3, and 40.2° for **XIVf**. Thus, the principal difference between molecules **XIIIf** and **XIVf** is the orientation of the epoxy group (*trans* or *cis*).

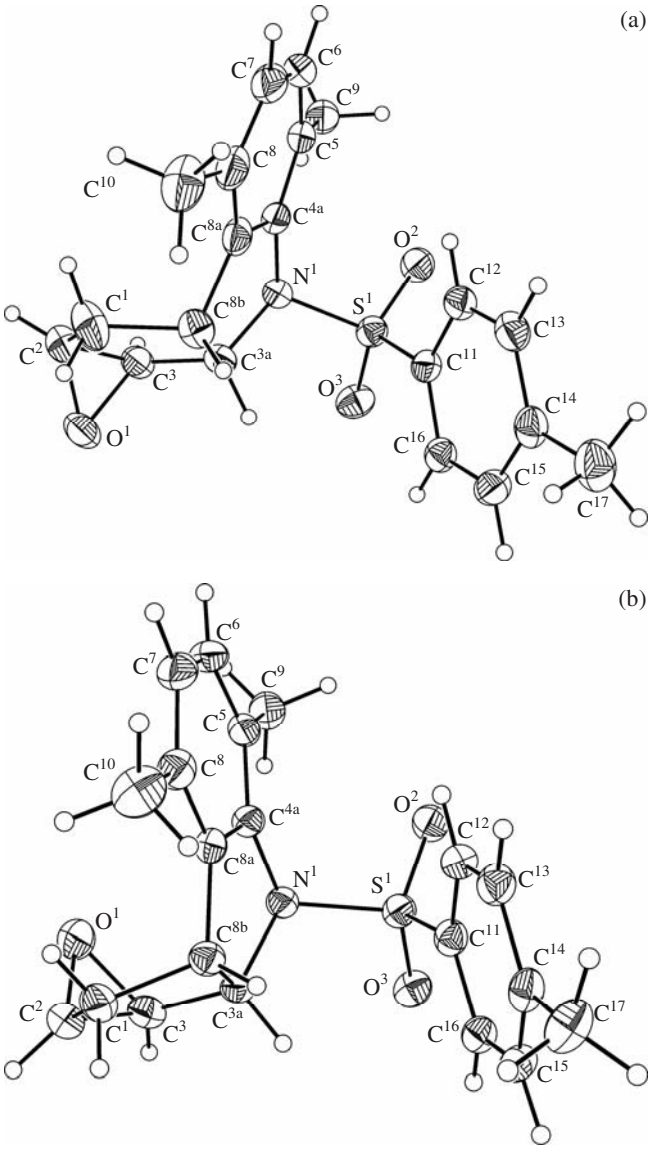


Fig. 1. Structures of molecules (a) **XIIIf** and (b) **XIVf** according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%.

The crystalline structures of both isomers **XIIIf** and **XIVf** lack any specific intermolecular interactions, and their molecules in crystal are linked through van der Waals forces; in addition, very weak C–H···O contacts were revealed, which can be regarded as intermediate between van der Waals interactions and normal hydrogen bonds [**XIIIf**: C^{16}–$H^{16a}\cdots O^2$: $C^{16}\cdots O^2$ 3.291(2), $H^{16a}\cdots O^2$ 2.67 Å, ∠CHO 123°; **XIVf**: C^{17}–$H^{17a}\cdots O^2$, $C^{17}\cdots O^2$ 3.370(2), $H^{17a}\cdots O^2$ 2.46 Å, ∠CHO 155°].

Some similarities were also found between crystal packings of compounds **XIIIf** and **XIVf**. The above weak C–H···O intermolecular contacts give rise to chains extended along the crystallographic *a* axis for *trans* isomer **XIIIf** and *b* axis for *cis* isomer **XIVf** (Figs. 2, 3). In both structures, the above contacts involve carbon atoms of the toluene fragment and similarly arranged oxygen atoms of the sulfonyl group. Some differences are observed in mutual orientations of their molecules within the chain and orientations of the neighboring chains. In the crystalline structure of **XIIIf**, molecules in a chain are related to each other through a plane orthogonal to the *c* axis, and in the structure of **XIVf**, through a second-order symmetry

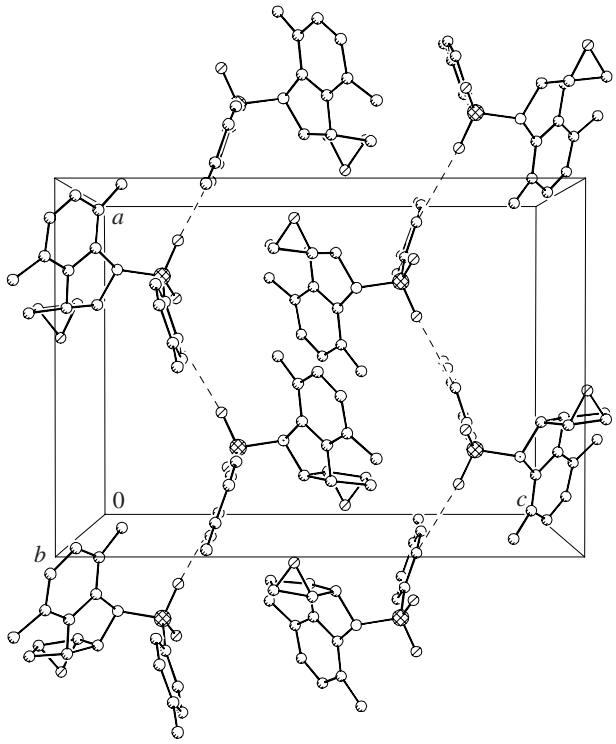


Fig. 2. A fragment of crystal packing of compound **XIIIf**.

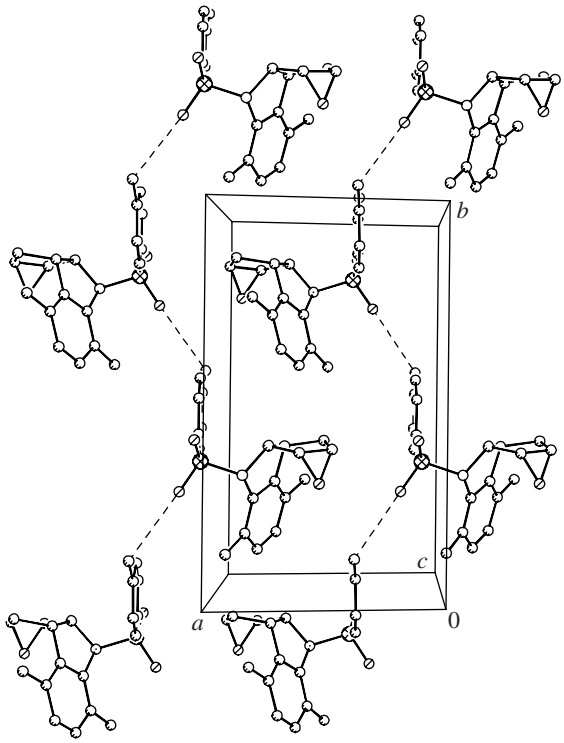


Fig. 3. A fragment of crystal packing of compound **XIVf**.

axis. The chain couples shown in Figs. 2 and 3 are related to each other through the 2_1 axis which is parallel to the crystallographic *c* axis for compound **XIIIf** and through translation along the *a* axis for isomer **XIVf**.

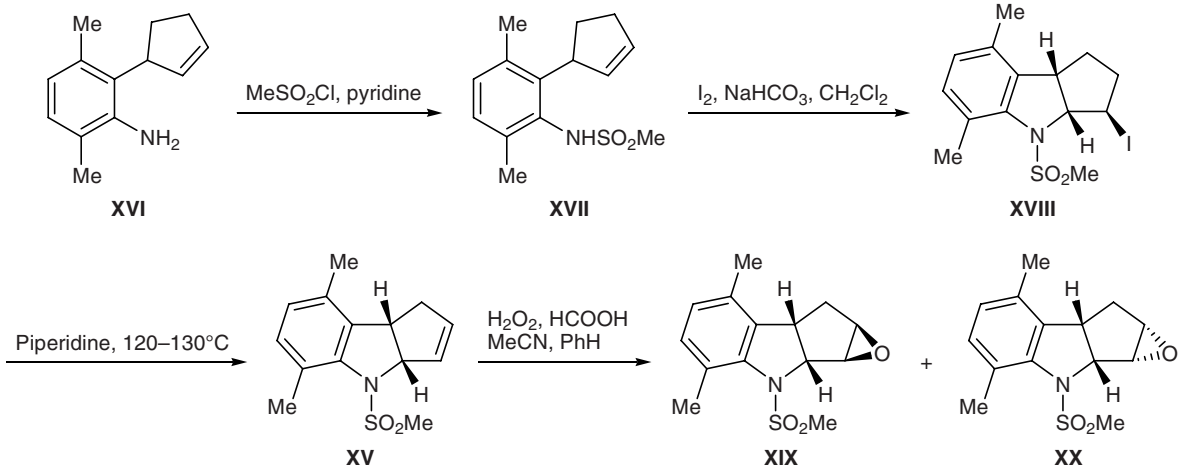
Analysis of the role of weak interactions in crystal is fairly complex [22], especially when the only intermolecular interactions are van der Waals or weak C–H···O contacts, as in the crystalline structures of **XIIIf** and **XIVf**. With a view to obtain more detailed information on their crystal packing, we calculated the energies of intramolecular interactions in terms of the atom–atom potential method using NONVPOT program [23] with Mirsky's parameterization [24]. In both structures, each molecule interacts most strongly with 4–5 neighboring molecules, thus forming a three-dimensional structure. This means that neither chains (columns) nor layers where interactions within a chain (layer) would be considerably stronger than those between different chains (layers) could be distinguished in the crystalline structures of **XIIIf** and **XIVf**. According to the calculations, the energies of the crystal packings differ by only 3 kcal/mol and are –26.6 and –29.6 kcal/mol for **XIIIf** and **XIVf**, respectively. The more energetically favorable structure of **XIVf** is characterized by slightly tighter packing (see table).

In order to elucidate how the size of the protecting group on the nitrogen atom affects the ratio of isomeric epoxy derivatives, we made an attempt to effect iodocyclization of *N*-(*p*-nitrophenylsulfonyl)-2-(2-cyclopenten-1-yl)-3,6-dimethylaniline having a bulkier protecting group. However, we failed to isolate the expected cyclization product, presumably for steric reasons. Therefore, we synthesized *N*-methylsulfonyltetrahydrocyclopenta[*b*]indole **XV** with a smaller N-substituent as compared to tosyl group. Compound **XV** was obtained according to Scheme 4 using 2-(cyclopent-2-en-1-yl)-3,6-dimethylaniline (**XVI**) [25] as starting material.

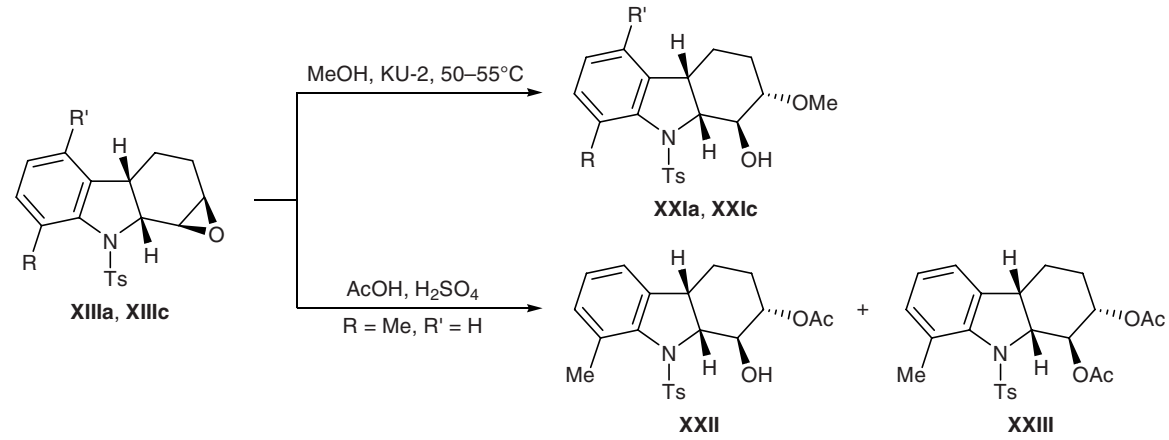
The oxidation of **XV** with hydrogen peroxide led to the formation of a mixture of approximately equal amounts of isomeric epoxy derivatives **XIX** and **XX**. The reactions of cyclohexene analogs **XIIa**–**XIIc** with H_2O_2 gave epoxides **XIIIa**–**XIIIc** which were separated from unreacted initial compounds **XIIa**–**XIIc** by column chromatography. The absence of products with *cis* orientation of the dihydropyrrole and oxirane rings was rationalized in terms of steric effect of an "extra" methylene group, which is well demonstrated by molecular modeling.

Heating of epoxy derivatives **XIIIa** and **XIIIc** in methanol in the presence of KU-2 cation exchanger resulted in *trans*-opening of the oxirane ring with formation of methoxy alcohols **XXIa** and **XXIc** in good yields (Scheme 5). The use of KU-2 in acetic

Scheme 4.



Scheme 5.



R = Me, R′ = H (**a**), R = R′ = Me (**c**).

acid to effect cleavage of **XIIIa** was unsuccessful. The reaction of **XIIIa** with acetic acid in the presence of sulfuric acid gave monoacetate **XXII** as a result of *trans*-opening of the oxirane ring. In addition, diacetate **XXIII** was isolated; presumably, the latter was formed via subsequent esterification of monoacetate **XXII**. Treatment of compound **XIIIf** in methanol in the presence of KU-2 afforded methoxy derivative **XXIV**. Under analogous conditions, from epoxides **XIVd** and **XIVf** we obtained the corresponding methoxy alcohols **XXVd** and **XXVf** in good yields (Scheme 6).

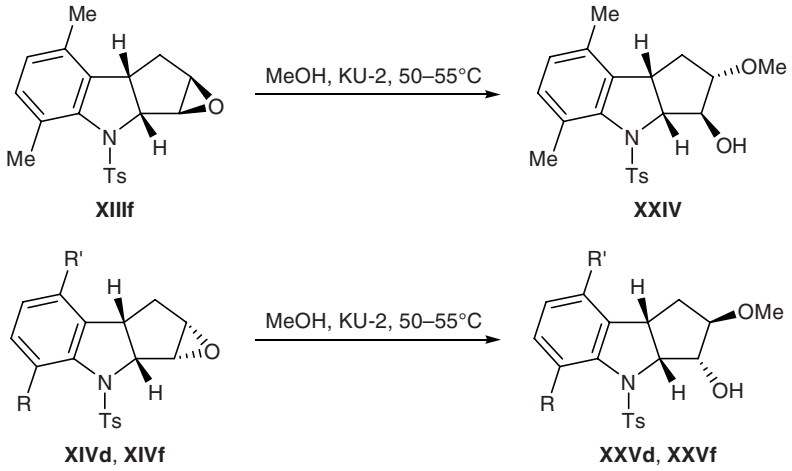
We can conclude that *N*-*p*-tolylsulfonyl-3,4,4a,9a-tetrahydrocarbazoles react with hydrogen peroxide to give the corresponding 1,2-epoxy-*N*-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazoles with high stereoselectivity. *N*-*p*-Tolylsulfonyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles give rise to mixtures of stereoisomeric 2,3-epoxy derivatives with *cis* and *trans* arrangement of the oxirane and nitrogen-containing rings.

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 tetramethylsilane as internal reference. The elemental compositions were determined on an M-185B CHN Analyzer. Column chromatography was performed on silica gel LS (40–100 μm; from Lancaster). Sorbfil plates (*Sorbpolimer* Ltd., Krasnodar, Russia) were used for qualitative TLC analysis; development with iodine vapor.

Single crystals of compounds **XIIIf** and **XIVf** were obtained by slow crystallization from 95% ethanol.

Scheme 6.



R = Me, R′ = H (**d**), R = R′ = Me (**f**).

The X-ray diffraction data were acquired on a SMART 1000 CCD diffractometer [λ(MoK_α) 0.71073 Å, graphite monochromator, ω-scanning] at 120 K. The principal crystallographic parameters are given in table. The sets of reflection intensities were processed using SAINT Plus [26] and SADABS programs [27]. The structures were solved by the direct method and were refined by the full-matrix least-squares procedures in anisotropic approximation for non-hydrogen atoms (with respect to F_{hkl}^2) using SHELXTL-97 software package [28]. The positions of hydrogen atoms were calculated from the geometry considerations and were refined using the riding model [$U_{iso}(H) = nU_{eq}(C)$, where n = 1.5 for methyl carbon atoms, and n = 1.2 for the other carbon atoms].

***N*-Benzoyl-1-iodo-8-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (VIIc).** A mixture of 0.29 g (1 mmol) of benzamide **VIc**, 0.84 g (10 mmol) of $NaHCO_3$, and 0.51 g (2 mmol) of I_2 in 20 ml of methylene chloride was stirred at room temperature until the initial benzamide disappeared. The mixture was diluted with 30 ml of methylene chloride and treated with 10% aqueous $Na_2S_2O_3$ (2×20 ml), and the organic phase was washed with water (2×10 ml), dried over $MgSO_4$, and evaporated under reduced pressure. Yield 0.4 g (96%), amorphous material, R_f 0.5 (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90–1.00 m (6H, CH_2), 2.20 s (3H, CH_3), 3.70–3.77 m (1H, 4a-H), 3.90 d.d.d (1H, 1-H, J_1 = 4.0, J_2 = 9.0, J_3 = 13.0 Hz), 5.00–5.03 m (1H, 9a-H), 7.00–7.05 m (8H, H_{arom}). Found, %: C 57.13; H 4.43; I 30.02; N 2.98. $C_{20}H_{20}INO$. Calculated, %: C 57.57; H 4.83; I 30.41; N 3.36.

1-Methyl-2a,3,4,5,5a,10a-hexahydro[1,3]oxazolo-[5,4,3-*jk*]carbazol-10-ium iodide (VIIIb). Compound **VIb**, 0.25 g (1.2 mmol), was subjected to iodocyclization [20]. After appropriate treatment, product **VIIb** was dissolved in 3 ml of benzene, and the solution was heated for 20 min under reflux. After cooling, the solvent was separated from the crystalline product by decanting. Yield 0.31 g (79%), colorless crystals, mp 175°C (from benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20–2.00 m (6H, CH_2), 2.1 s (3H, CH_3), 3.19 d.t (1H, 5a-H, J_1 = 6.2, J_2 = 10.7 Hz), 4.00 d.d (1H, 10a-H, J_1 = 4.8, J_2 = 6.4 Hz), 5.11 d.d.d (1H, 2a-H, J_1 = 6.4, J_2 = 6.7, J_3 = 15.2 Hz), 6.90–7.20 m (4H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.2, 25.6, 29.0 (CH_2); 21.8 (CH_3); 41.3 (C^{5a}); 60.5 (C^{10a}); 72.9 (C^{2a}); 109.7, 117.7, 122.9, 127.2, 134.5, 150.5 (C_{arom}); 170.1 (N^+=C–O). Found, %: C 48.97; H 4.44; I 36.82; N 3.76; anionic iodine: 36.12%. $C_{19}H_{18}INO$. Calculated, %: C 49.28; H 4.73; I 37.19; N 4.11.

9-Methyl-1-phenyl-2a,3,4,5,5a,10a-hexahydro-[1,3]oxazolo[5,4,3-*jk*]carbazol-10-ium iodide (VIIIc). A mixture of 0.42 g (1 mmol) of compound **VIIc** and 3 ml of benzene was heated for 20 min under reflux. After cooling, the precipitate was filtered off. Yield 0.37 g (88%), colorless crystals, mp 157–159°C. IR spectrum, ν, cm^{-1}: 1725, 1475, 1375, 1270, 1115, 1035, 775, 725. UV spectrum (MeCN): λ_{max} 365, $\lambda_{min.}$ 330 nm. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.20–2.39 m (6H, CH_2), 2.40 s (3H, CH_3), 3.70 d.t (1H, 5a-H, J_1 = 6.2, J_2 = 8.8 Hz), 4.70 d.d (1H, 10a-H, J_1 = 4.6, J_2 = 6.2 Hz), 5.65 d.d.d (1H, 2a-H, J_1 = 4.6, J_2 = 4.9, J_3 = 9.2 Hz), 7.00–7.60 m (8H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.6 (CH_3); 18.4, 26.6, 26.7 (CH_2); 40.6 (C^{5a}); 61.4 (C^{10a}); 70.3 (C^{2a}); 120.9,

Crystallographic data for compounds **XIIIf** and **XIVf** and parameters of X-ray diffraction experiments

Parameter	**VIIIf**	**IXf**
Formula	$C_{20}H_{21}NO_3S$	$C_{20}H_{21}NO_3S$
Molecular weight	355.44	355.44
Color and shape of crystal	Colorless prism	Colorless prism
Crystal habit, mm	0.30×0.25×0.20	0.20×0.15×0.10
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
a, Å	12.4398(9)	8.7077(6)
b, Å	16.3531(11)	14.3510(9)
c, Å	17.3960(13)	14.3817(9)
β, deg	90	104.24(10)
Z	8	4
V, Å^3	3538.9(4)	1741.9(2)
d_{calc}, mg/m^3	1.334	1.355
Absorption coefficient μ, mm^{-1}	0.202	0.205
F(000)	1504	752
Scan range θ, deg	2.34–27.00	2.04–27.00
Total number of reflections	18886	14990
Number of independent reflections	3821	3755
R_{int}	0.0284	0.0301
Number of refined parameters	229	229
Number of reflections with $I > 2\sigma(I)$	3029	3030
Completeness of reflection set, %	98.9	99.0
Goodness of fit	1.036	1.005
Divergence factor $R_1(F)$[a] for reflections with $I > 2\sigma(I)$[a]	0.0452	0.0420
Divergence factor $wR_2(F^2)$[b] for all reflections	0.0932	0.0874
Residual electron density, max/min, *e*/Å^3	0.460/–0.336	0.374/–0.332

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

128.2, 129.6, 129.7, 129.8, 133.1 (C^6, C^7, C^8, $C^{2'}/C^{6'}$, $C^{3'}/C^{5'}$, $C^{4'}$); 127.5, 129.2, 137.0, 137.7, 165.7 (C^{5b}, C^9, C^{9a}, $C^{1'}$, N^+=C–O). Found, %: C 57.28; H 3.04; I 30.02; N 3.05; anionic iodine: 29.98%. $C_{20}H_{20}INO$. Calculated, %: C 57.57; H 4.83; I 30.41; N 3.36.

***N*-Acetyl-3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (X).** Acetic anhydride, 0.27 ml (4.5 mmol), was added under stirring to a solution of 0.9 g (3.15 mmol) of compound **IX** [19] in 3 ml of chloroform, and the mixture was left to stand for 24 h at room temperature. When the reaction was complete, the mixture was treated with a 10% solution of $NaHCO_3$ (2×50 ml) and extracted with chloroform (2×50 ml). The organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure, and the residue was recrystallized from hexane. Yield 0.83 g (80%), colorless crystals, mp 123–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.60–1.80 m (1H, 2-H), 1.90–2.15 m (2H, CH_2), 2.45 s (3H, CH_3), 2.55–2.70 m (1H, 2-H), 4.00 t (1H, 8b-H, *J* = 8.0 Hz), 4.40 d (1H, 3-H, *J* = 4.2 Hz), 5.07 d (1H, 3a-H, *J* = 8.0 Hz), 6.80–7.03 m (4H, H_{arom}). Found, %: C 47.45; H 3.94; I 38.48; N 4.01. $C_{13}H_{14}INO$. Calculated, %: C 47.73; H 4.31; I 38.79; N 4.28.

***N*-Acetyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (XI).** Compound **X**, 0.33 g (1 mmol), was heated in dimethylformamide for 4 h at 180°C. When the reaction was complete, the solvent was distilled off under reduced pressure, the residue was dissolved in 50 ml of methylene chloride, the solution was washed

with water (2×20 ml), dried over Na_2SO_4, and evaporated under reduced pressure, and the residue was recrystallized from hexane. Yield 0.14 g (70%), colorless crystals, mp 105–108°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 2.60 d.t (1H, 1-H_A, J_1 = 1.8, J_2 = 17.1 Hz), 3.00 d.d.d.t (1H, 1-H_B, J_1 = 1.8, J_2 = 2.7, J_3 = 8.3, J_4 = 17.1 Hz), 4.10 t.d (1H, 8b-H, J_1 = 1.8, J_2 = 8.3 Hz), 5.30 d.q (1H, 3a-H, J_1 = 1.8, J_2 = 8.3 Hz), 5.90 d.t (1H, 2-H, J_1 = 1.8, J_2 = 6.0 Hz), 6.00 d.t (1H, 3-H, J_1 = 1.8, J_2 = 6.0 Hz), 7.00–7.20 m (3H, H_{arom}), 8.10 d (1H, 5-H, J = 8.0 Hz). Found, %: C 78.05; H 6.26; N 6.81. $C_{13}H_{13}NO$. Calculated, %: C 78.36; H 6.58; N 7.03.

Epoxy derivatives XIIIa–XIIIc and XIVd–XIVf. A solution of 3 mmol of compound **XIIa**–**XIIf** in 80 ml of benzene was added to a mixture of 6 ml of formic acid and 5 ml of 33% hydrogen peroxide, 135 ml of acetonitrile was then added, and the mixture was heated for 16–17 h at 50–60°C. After cooling to room temperature, the mixture was washed with 10% aqueous $NaHCO_3$ until carbon dioxide no longer evolved and with water (3×50 ml). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure, and the residue was recrystallized from ethanol (compounds **XIIIa**–**XIIIc**) or subjected to chromatography on silica gel using benzene as eluent to isolate epoxides **XIIId**–**XIIIf** and **XIVd**–**XIVf**.

(1*S*,2*R*,4a*S*,9a*R*)-2,3-Epoxy-8-methyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazole (XIIIa). Yield 0.89 g (84%), colorless crystals, mp 175–177°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.05–1.65 m (4H, CH_2), 2.15 m (4H, 4a-H, CH_3), 2.51 s (3H, CH_3), 2.67 m (1H, 2-H), 3.02 d (1H, 1-H, J = 3.5 Hz), 4.39 d (1H, 9a-H, J = 8.0 Hz), 6.50 d (1H, H_{arom}, J = 7.2 Hz), 6.82–7.25 m (6H, H_{arom}). Found, %: C 67.63; H 6.02; N 3.89; S 8.95. $C_{20}H_{21}NO_3S$. Calculated, %: C 67.58; H 5.95; N 3.95; S 9.02.

(1*S*,2*R*,4a*S*,9a*R*)-2,3-Epoxy-8-methoxy-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazole (XIIIb). Yield 0.56 g (50%), colorless crystals, mp 159–161°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.10–1.75 m (4H, CH_2), 2.20 s (3H, CH_3), 2.70 m (2H, 2-H, 4a-H), 2.90 d (1H, 1-H, J = 3.6 Hz), 3.67 s (3H, OCH_3), 4.62 d (1H, 9a-H, J = 7.1 Hz), 6.40 d (1H, H_{arom}, J = 7.4 Hz), 6.63 d (1H, H_{arom}, J = 7.5 Hz), 6.90 m (3H, H_{arom}), 7.45 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 64.83; H 5.52; N 3.80; S 8.75. $C_{20}H_{21}NO_4S$. Calculated, %: C 64.67; H 5.70; N 3.77; S 8.63.

(1*S*,2*R*,4a*S*,9a*R*)-2,3-Epoxy-5,8-dimethyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazole (XIIIc). Yield 0.75 g (68%), colorless crystals, mp 156–159°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.00–2.00 m (4H, CH_2); 1.90 s, 2.15 s, and 2.45 s (3H each, CH_3); 2.20 m (1H, 4a-H); 2.70 m (1H, 1-H); 3.05 d (1H, 2-H, J = 3.6 Hz); 4.30 d (1H, 9a-H, J = 7.7 Hz); 6.65 d (1H, H_{arom}, J = 7.7 Hz); 6.85 d (2H, H_{arom}, J = 8.3 Hz); 7.05–7.15 m (3H, H_{arom}). ^{13}C NMR spectrum (C_6D_6–CCl_4), δ_C, ppm: 15.7, 19.9 (C^3, C^4); 19.3, 20.1, 20.8 (CH_3); 38.0 (C^{4a}); 51.0 (C^2); 53.6 (C^1); 60.4 (C^{9a}); 128.5, 128.8, 129.2, 130.9 (C^6, C^7, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 130.2, 131.2, 135.4, 135.5, 142.2, 143.3 (C^{4b}, C^5, C^8, C^{8a}, $C^{1'}$, $C^{4'}$). Found, %: C 68.63; H 6.15; N 3.89; S 8.55. $C_{21}H_{23}NO_3S$. Calculated, %: C 68.27; H 6.27; N 3.79; S 8.68.

(2*R*,3*S*,3a*R*,8b*S*)-2,3-Epoxy-5-methoxy-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIIId). Yield 0.27 g (26%), colorless crystals, mp 119–121°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.60 d.d.d (1H, 1-H_A, J_1 = 2.2, J_2 = 4.2, ^2J = 14.4 Hz), 2.28 s (3H, CH_3), 2.32 d.d (1H, 1-H_B, J_1 = 8.3, ^2J = 14.4 Hz), 3.26 t (1H, 2-H, J = 2.2 Hz), 3.40 d.t (1H, 8b-H, J_1 = 4.2, J_2 = 8.3 Hz), 3.49 s (3H, CH_3), 3.72 d (1H, 3-H, J = 2.2 Hz), 4.97 d (1H, 3a-H, J = 8.3 Hz), 6.50 d (1H, H_{arom}, J = 7.5 Hz), 6.54 d (1H, H_{arom}, J = 8.3 Hz), 6.83 t (1H, 7-H, J = 7.9 Hz), 7.05 d (2H, H_{arom}, J = 8.3 Hz), 7.60 d (2H, H_{arom}, J = 8.3 Hz). Found, %: C 63.63; H 5.25; N 3.89; S 8.95. $C_{19}H_{19}NO_4S$. Calculated, %: C 63.85; H 5.36; N 3.92; S 8.97.

(2*R*,3*S*,3a*R*,8b*S*)-2,3-Epoxy-5,8-dimethyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIIIf). Yield 0.38 g (36%), colorless crystals, mp 134–136°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.45 d.t (1H, 1-H_A, J_1 = 2.5, ^2J = 14.3 Hz), 1.95 s (3H, CH_3), 2.20 d.d (1H, 1-H_B, J_1 = 8.7, ^2J = 14.3 Hz), 2.26 s (3H, CH_3), 2.60 s (3H, CH_3), 2.90 d.t (1H, 8b-H, J_1 = 2.5, J_2 = 7.7 Hz), 3.15 m (1H, 3-H), 3.70 m (1H, 2-H), 4.45 d (1H, 3a-H, J = 7.7 Hz), 6.75 d (1H, H_{arom}, J = 7.6 Hz), 6.90–7.00 m (3H, H_{arom}), 7.15 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 67.53; H 6.02; N 3.99; S 8.95. $C_{20}H_{21}NO_3S$. Calculated, %: C 67.58; H 5.95; N 3.95; S 9.02.

(2*S*,3*R*,3a*S*,8b*S*)-2,3-Epoxy-5-methyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIVd). Yield 0.3 g (29%), colorless crystals, mp 182–184°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.70 d.d.d (1H, 1-H_A, J_1 = 2.0, J_2 = 9.0, J_3 = 14.5 Hz), 1.93 d (1H, 1-H_B, J = 14.5 Hz), 2.22 s (3H, CH_3), 2.55 s (3H, CH_3), 3.13 m (1H, 3-H), 3.58 t (1H, 8b-H), 4.47 d.d (1H, 3a-H, J_1 = 2.0, J_2 =

8.1 Hz), 6.60 d (1H, H_{arom}, J = 7.7 Hz), 6.70–7.05 m (3H, H_{arom}), 7.20 d (2H, H_{arom}, J = 8.3 Hz). Found, %: C 66.92; H 5.62; N 4.15; S 9.48. $C_{19}H_{19}NO_3S$. Calculated, %: C 66.84; H 5.61; N 4.10; S 9.39.

(2*S*,3*R*,3a*S*,8b*S*)-2,3-Epoxy-5-methoxy-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-cyclopenta[*b*]indole (XIVe). Yield 0.33 g (31%), colorless crystals, mp 172–174°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.99 d (1H, 1-H_A, J_1 = 9.3, ^2J = 12.8 Hz), 2.12 d (1H, 1-H_B, ^2J = 12.8 Hz), 2.30 s (3H, CH_3), 3.29 m (1H, 3-H), 3.45–3.52 m (4H, OCH_3, 8b-H), 3.62 m (1H, 2-H), 5.00 d (1H, 3a-H, J = 8.8 Hz), 6.40 d (1H, H_{arom}, J = 7.7 Hz), 6.54 d (1H, H_{arom}, J = 8.0 Hz), 6.80 d.d (1H, H_{arom}, J_1 = 7.7, J_2 = 8.0 Hz), 7.05 d (2H, H_{arom}, J = 7.85 Hz), 7.60 d (2H, H_{arom}, J = 7.8 Hz). Found, %: C 63.75; H 5.45; N 3.99; S 8.95. $C_{19}H_{19}NO_4S$. Calculated, %: C 63.85; H 5.36; N 3.92; S 8.97.

(2*S*,3*R*,3a*R*,8b*S*)-2,3-Epoxy-5,8-dimethyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (XIVf). Yield 0.39 g (37%), colorless crystals, mp 123–125°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.69 d.d.d (1H, 1-H_A, J_1 = 1.0, J_2 = 8.0, ^2J = 13.5 Hz), 1.90 s (3H, CH_3), 2.03 d (1H, 1-H_B, ^2J = 13.5 Hz), 2.20 s (3H, CH_3), 2.50 s (3H, CH_3), 2.63 t (1H, 8b-H, J = 8.0 Hz), 3.15 m (1H, 3-H), 3.55 m (1H, 2-H), 4.50 d.d (1H, 3a-H, J_1 = 2.0, J_2 = 8.0 Hz), 6.69 d (1H, H_{arom}, J = 7.7 Hz), 6.80–6.95 m (3H, H_{arom}), 7.11 d (2H, H_{arom}, J = 7.9 Hz). Found, %: C 67.61; H 6.00; N 3.99; S 9.05. $C_{20}H_{21}NO_3S$. Calculated, %: C 67.58; H 5.95; N 3.95; S 9.02.

4-Methylsulfonyl-5,8-dimethyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (XV). Methanesulfonyl chloride, 5.15 g (45 mmol), was added to a solution of 5.61 g (30 mmol) of 2-(cyclopent-2-en-1-yl)-3,6-dimethylaniline (**XVI**) [25] in 15 ml of pyridine. After 24 h, the mixture was diluted with 200 ml of methylene chloride and washed with 5% hydrochloric acid to remove pyridine and water (25 ml), and the organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was 7.32 g (92%) of crude compound **XVII** as a viscous material, R_f 0.48 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.80–2.55 m (4H, CH_2), 2.29 s (3H, CH_3), 2.42 s (3H, CH_3), 3.03 s (3H, CH_3), 4.82–4.92 m (1H, CH), 5.69–5.73 m (1H, C=CH), 5.77–5.82 m (1H, HC=C), 6.95 d (1H, H_{arom}, J = 7.8 Hz), 7.03 d (1H, H_{arom}, J = 7.8 Hz), 7.75 br.s (NH).

Compound **XVII** was mixed with 13.96 g (55 mmol) of I_2 in 100 ml of methylene chloride and 23.18 g (276 mmol) of $NaHCO_3$, and the mixture was stirred until initial compound **XVII** disappeared, washed with an aqueous solution of $Na_2S_2O_3$ and water (20 ml), dried over $MgSO_4$, and evaporated to obtain 10.58 g (98%) of compound **XVIII** as an oily substance, R_f 0.69 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.64–1.78 m (1H, 1-H_A), 1.98–2.11 m (2H, 1-H_B, 2-H_A), 2.42–2.52 m (1H, 2-H_B), 2.30 s (3H, CH_3), 2.40 s (3H, CH_3), 2.97 s (3H, CH_3), 4.01–4.14 m (2H, 8b-H, 3-H), 5.04 d.d (1H, 3a-H, J_1 = 6.8, J_2 = 8.4 Hz), 6.99 d (1H, 7-H, J = 7.7 Hz), 7.40 d (1H, 6-H, J = 7.7 Hz).

Compound **XVIII** was dissolved in 80 ml of piperidine, and the mixture was heated for 8 h at the boiling point. Piperidine was distilled off under reduced pressure, the residue was dissolved in 200 ml of methylene chloride, the solution was washed with water (3× 30 ml) and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol. Yield of **XV** 7.1 g (60% on the initial compound **XVI**), colorless crystals, mp 117–119°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.18 s (3H, CH_3), 2.21 s (3H, CH_3), 2.38 d.q (1H, 1-H_A, J_1 = 2.2, ^2J = 18.4 Hz), 2.70 s (3H, CH_3), 2.79 d.d.q (1H, 1-H_B, J_1 = 2.2, J_2 = 8.0, ^2J = 18.4 Hz), 4.18 d.t (1H, 8b-H, J_1 = 7.7, J_2 = 8.0 Hz), 5.35 d.q (1H, 3a-H, J_1 = 2.2, J_2 = 7.7 Hz), 5.57 m (1H, 2-H), 5.67 m (1H, 3-H), 6.80 d (1H, H_{arom}, J = 7.8 Hz), 6.90 d (1H, H_{arom}, J = 7.8 Hz). Found, %: C 63.63; H 6.02; N 5.19; S 12.05. $C_{14}H_{17}NO_2S$. Calculated, %: C 63.85; H 6.51; N 5.31; S 12.18.

Epoxidation of *N*-methylsulfonyl derivative XV. A solution of 0.79 g (3 mmol) of compound **XV** in 80 ml of benzene was added to a mixture of 6 ml of formic acid and 5 ml of 33% hydrogen peroxide, 135 ml of acetonitrile was then added, and the mixture was heated for 17 h at 50–60°C. After cooling to room temperature, the mixture was washed with a 10% aqueous solution of $NaHCO_3$ until carbon dioxide no longer evolved and with water (3×50 ml). The organic phase was separated, dried over $MgSO_4$, and evaporated under reduced pressure, and the residue, a mixture of *cis* and *trans* isomers **XIV** and **XV**, was separated by chromatography on silica gel using benzene as eluent.

(2*R*,3*S*,3a*R*,8b*S*)-2,3-Epoxy-5,8-dimethyl-4-methylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta-[*b*]indole (XIX). Yield 0.25 g (30%), colorless crystals, mp 129–131°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.50 d.d (1H, 1-H_A, J_1 = 2.0, ^2J = 14.0 Hz), 2.10 s (3H, CH_3), 2.35 s (3H, CH_3), 2.40–

2.55 m (4H, CH_3, 1-H_B), 3.27 m (1H, 3-H), 3.12 m (1H, 2-H), 3.20 m (1H, 8b-H), 4.60 d (1H, 3a-H, J = 8.2 Hz), 6.71 d (1H, H_{arom}, J = 7.4 Hz), 6.85 d (1H, H_{arom}, J = 7.4 Hz). Found, %: C 60.03; H 6.02; N 4.99; S 11.45. $C_{14}H_{17}NO_3S$. Calculated, %: C 60.19; H 6.13; N 5.01; S 11.48.

(2*S*,3*R*,3a*R*,8b*S*)-2,3-Epoxy-5,8-dimethyl-4-methylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta-[*b*]indole (XX). Yield 0.21 g (26%), colorless crystals, mp 147–149°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.15–2.30 m (4H, CH_3, 1-H_A), 2.40–2.49 m (1H, 1-H_B), 2.70 s (3H, CH_3), 2.50 s (3H, CH_3), 3.55 m (1H, 3-H), 3.84 t (1H, 2-H, J = 2.0 Hz), 4.05 t (1H, 8b-H, J = 8.7 Hz), 4.95 d.d (1H, 3a-H, J_1 = 2.0, J_2 = 8.7 Hz), 6.87 d (1H, H_{arom}, J = 7.7 Hz), 6.98 d (1H, H_{arom}, J = 7.7 Hz). Found, %: C 60.13; H 6.22; N 5.05; S 11.45. $C_{14}H_{17}NO_3S$. Calculated, %: C 60.19; H 6.13; N 5.01; S 11.48.

Hexahydrocarbazoles XXIa and XXIc (*general procedure*). Epoxy derivative **XIIIa** or **XIIIc**, 0.6 mmol, was dissolved in 8 ml of benzene, and 20 ml of methanol and 1 g of KU-2 cation exchanger were added. The mixture was stirred for 16 h at 40–50°C and cooled to room temperature, KU-2 was filtered off and washed with methylene chloride on a filter, the solvent was distilled off from the filtrate under reduced pressure, and the residue was recrystallized from ethanol.

(1*S*,2*R*,4a*S*,9a*R*)-2-Methoxy-8-methyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazol-1-ol (XXIa). Yield 0.22 g (96%), colorless crystals, mp 157–159°C (from EtOH). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 0.80 d.t (1H, 3-H_{ax}, J_1 = 3.8, J_2 = 13.5 Hz), 1.35 d.t (1H, 4-H_{ax}, J_1 = 3.8, J_2 = 14.0 Hz), 1.55 d (1H, 3-H_{eq}, J = 13.5 Hz), 1.80 d (1H, 4-H_{eq}, J = 14.0 Hz), 2.20 s (3H, CH_3), 2.40 s (3H, CH_3), 2.60 m (1H, 4a-H), 2.75 d.t (1H, 2-H, J_1 = 3.8, J_2 = 10.0 Hz), 3.00 t (1H, 1-H, J_1 = 8.0, J_2 = 10.0 Hz), 3.14 s (3H, CH_3), 4.00 t (1H, 9a-H, J_1 = 7.4, J_2 = 9.5 Hz), 6.55 d (1H, H_{arom}, J = 7.0 Hz), 6.90 m (4H, H_{arom}), 7.45 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 65.02; H 6.42; N 3.59; S 8.25. $C_{21}H_{25}NO_4S$. Calculated, %: C 65.09; H 6.50; N 3.61; S 8.28.

(1*S*,2*R*,4a*S*,9a*R*)-2-Methoxy-5,8-dimethyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazol-1-ol (XXIc). Yield 0.21 g (89%), amorphous material, R_f 0.14 (C_6H_6–EtOAc, 9:1). ^{1}H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.11 d.d.t (1H, 3-H_{ax}, J_1 = 3.8, J_2 = 10.0, ^2J = 13.5 Hz), 1.30 s (1H, OH), 1.57 m (1H, 4-H_{ax}), 2.00 q.d (1H, 3-H_{eq}, J_1 = 3.8, J_2 = 13.5 Hz), 2.10 s (3H, CH_3), 2.30 s (3H, CH_3), 2.37 d.q.d (1H, 4-H_{eq}, J_1 = 2.0, J_2 = 3.8, J_3 = 13.5 Hz), 2.50 s (3H, CH_3), 2.70 d.d.d (1H, 2-H, J_1 = 3.8, J_2 = 9.5, J_3 = 11.0 Hz), 3.10 d.d (1H, 1-H, J_1 = 8.1, J_2 = 9.5 Hz), 3.24 d.d.d (1H, 4a-H, J_1 = 2.0, J_2 = 6.0, J_3 = 7.5 Hz), 3.35 s (3H, OCH_3), 3.95 d.d (1H, 9a-H, J_1 = 7.5, J_2 = 9.5 Hz), 6.23 d (1H, H_{arom}, J = 7.7 Hz), 6.93 d (1H, H_{arom}, J = 7.7 Hz), 7.05 d (2H, H_{arom}, J = 8.0 Hz), 7.45 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 65.63; H 6.82; N 3.40; S 7.95. $C_{22}H_{27}NO_4S$. Calculated, %: C 65.81; H 6.78; N 3.49; S 7.99.

Reaction of epoxide XIIIa with acetic acid. A solution of 0.21 g (0.6 mmol) of compound **XIIIa**, 13 ml of acetic acid, and a catalytic amount of sulfuric acid was heated for 6 h at 50–60°C. The mixture was then cooled, 30 ml of methylene chloride and 30 ml of water were added, and the products were extracted into methylene chloride (3×25 ml). The extracts were washed with 10% aqueous $NaHCO_3$ and water (2×25 ml), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was recrystallized from ethanol to isolate diacetate **XXIII**. The mother liquor was evaporated under reduced pressure to obtain 0.11 g of crude compound **XXII** which was purified by recrystallization from 2 ml of carbon tetrachloride.

(1*S*,2*S*,4a*S*,9a*R*)-1-Hydroxy-8-methyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazol-2-yl acetate (XXII). Yield 0.07 g (27%), colorless crystals, mp 99–101°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02–2.03 m (4H, CH_2); 1.90 br.s (1H, OH); 2.10 s, 2.40 s, and 2.55 s (3H each, CH_3); 2.75 m (1H, 4a-H); 3.50 d.d.d (1H, 2-H, J_1 = 4.0, J_2 = 10.0, J_3 = 11.4 Hz); 4.20 d.d (1H, 9a-H, J_1 = 6.9, J_2 = 9.0 Hz); 4.25 d.d (1H, 1-H, J_1 = 9.0, J_2 = 11.4 Hz); 6.80 d (1H, H_{arom}, J = 6.3 Hz); 7.15 d (1H, H_{arom}, J = 6.3 Hz); 7.20 d (2H, H_{arom}, J = 8.2 Hz); 7.52 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.4, 21.0, 21.5 (CH_3); 21.7, 28.2 (CH_2); 40.0 (C^{4a}); 69.4, 70.6, 76.4 (C^1, C^2, C^{9a}); 119.6, 126.9, 127.4, 129.5, 130.7 (C^5, C^6, C^7, $C^{2'}$/$C^{6'}$, $C^{3'}$/$C^{5'}$); 134.2, 136.0, 138.2, 140.7, 143.9 (C^{4b}, C^8, C^{8a}, $C^{1'}$, $C^{4'}$), 171.4 (C=O). Found, %: C 63.62; H 6.02; N 3.42; S 7.95. $C_{22}H_{25}NO_5S$. Calculated, %: C 63.59; H 6.06; N 3.37; S 7.72.

(1*S*,2*S*,4a*S*,9a*R*)-8-Methyl-9-*p*-tolylsulfonyl-1,2,3,4,4a,9a-hexahydrocarbazole-1,2-diyl diacetate (XXIII). Yield 0.13 g (47%), colorless crystals, mp 170–172°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–2.10 m (4H, CH_2); 1.95 s, 2.05 s, 2.43 s, and 2.54 s (3H each, CH_3); 2.76 t (1H, 4a-H, J = 7.0 Hz); 4.17 d.d (1H, 9a-H, J_1 = 7.0, J_2 =

7.3 Hz); 4.65 m (2H, 1-H, 2-H); 6.73 d (1H, H_{arom}, J = 6.0 Hz); 7.10–7.20 m (4H, H_{arom}); 7.52 d (2H, H_{arom}, J = 8.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.3, 20.7, 20.8, 21.5 (CH_3); 21.6, 25.2 (CH_2); 39.9 (C^{4a}); 69.4, 71.6, 72.3 (C^1, C^2, C^{9a}); 119.5, 126.9, 130.8 (C^6, C^7, C^8); 127.4, 129.5 ($C^{2'}/C^{6'}$, $C^{3'}/C^{5'}$); 134.4, 135.9, 137.9, 140.7, 144.0 (C^{4b}, C^8, C^{8a}, $C^{1'}$, $C^{4'}$); 170.1, 170.2 (C=O). Found, %: C 63.05; H 6.02; N 3.09; S 7.10. $C_{24}H_{27}NO_6S$. Calculated, %: C 63.00; H 5.95; N 3.06; S 7.01.

Reaction of epoxides XIIIf, XIVd, and XIVf with methanol (*general procedure*). Compound **XIIIf**, **XIVd**, or **XIVf**, 0.4 mmol, was dissolved in 3 ml of benzene, 13 ml of methanol and 0.6 g of KU-2 cation exchanger were added, and the mixture was stirred for 6 h at 40–50°C, cooled, and filtered from KU-2, the precipitate was washed on a filter with methylene chloride, the filtrate was evaporated under reduced pressure, and the residue was recrystallized from ethanol.

(2*S*,3*S*,3a*R*,8b*S*)-2-Methoxy-5,8-dimethyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-3-ol (XXIV). Yield 0.14 g (90%), colorless crystals, mp 128–130°C (from EtOH). ^1H NMR spectrum (C_6D_6–CCl_4), δ, ppm: 1.10–1.22 m (1H, 1-H_A), 1.82 s (3H, CH_3), 2.07–2.21 m (1H, 1-H_B), 2.15 s (3H, CH_3), 2.42 s (3H, CH_3), 2.44–2.56 m (1H, 8b-H), 3.18 s (3H, OCH_3), 3.33 q (1H, 2-H, J = 8.2 Hz), 3.70 t (1H, 3-H, J = 7.7 Hz), 4.05 d (1H, 3a-H, J_1 = 7.7, J_2 = 8.2 Hz), 6.65 d (1H, H_{arom}, J = 7.6 Hz), 6.80–6.90 d (3H, H_{arom}), 7.15 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 64.93; H 6.62; N 3.59; S 8.35. $C_{21}H_{25}NO_4S$. Calculated, %: C 65.09; H 6.50; N 3.61; S 8.28.

(2*R*,3*R*,3a*R*,8b*S*)-2-Methoxy-5-methyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-3-ol (XXVd). Yield 0.14 g (74%), amorphous material, R_f 0.21 (C_6H_6–EtOAc, 9:1). ^1H NMR spectrum (C_6D_6), δ, ppm: 1.55–2.00 m (2H, CH_2); 2.20 s, 2.55 s, and 3.20 s (3H each, CH_3); 2.70 q (1H, 8b-H, J = 9.0 Hz); 3.15 m (1H, 2-H); 4.09 d.d (1H, 3-H, J_1 = 3.6, J_2 = 6.3 Hz); 4.48 d.d (1H, 3a-H, J_1 = 6.3, J_2 = 8.1 Hz); 6.65 d (1H, H_{arom}, J = 7.3 Hz); 6.90–7.10 m (4H, H_{arom}); 7.20 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 64.63; H 6.02; N 3.79; S 8.55. $C_{20}H_{23}NO_4S$. Calculated, %: C 64.32; H 6.21; N 3.75; S 8.59.

(2*R*,3*R*,3a*R*,8b*S*)-2-Methoxy-5,8-dimethyl-4-*p*-tolylsulfonyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-3-ol (XXVe). Yield 0.12 g (76%), amorphous material, R_f 0.07 (C_6H_6–EtOAc, 9:1). ^1H NMR spectrum (CCl_4–C_6D_6), δ, ppm: 1.20 s (1H, OH), 1.50 d.t (1H, 1-H_A, J_1 = 6.0, J_2 = 12.0 Hz), 1.90–2.10 m (1H, 1-H_B), 1.95 s (3H, CH_3), 2.20 s (3H, CH_3), 2.50 s (3H, CH_3), 2.78 q (1H, 8b-H, J = 9.0 Hz), 3.20 s (3H, OCH_3), 3.35–3.40 m (1H, 2-H), 4.16 d (1H, 3-H, J = 5.5 Hz), 4.45 d.d (1H, 3a-H, J_1 = 5.5, J_2 = 9.0 Hz), 6.70 d (1H, H_{arom}, J = 7.5 Hz), 6.89 d (1H, H_{arom}, J = 7.5 Hz), 6.92 d (2H, H_{arom}, J = 8.1 Hz), 7.12 d (2H, H_{arom}, J = 8.1 Hz). Found, %: C 65.03; H 6.52; N 3.55; S 8.35. $C_{21}H_{25}NO_4S$. Calculated, %: C 65.09; H 6.50; N 3.61; S 8.28.

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