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Reactions of *N*- and *C*-Alkenylanilines: X.* Synthesis of 2-Vinyldihydroindoles from 4-Methyl-2-(pent-3-en-2-yl)aniline

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Abstract—2-(1-Iodoethyl)-3,5-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole reacted with pyridine, piperidine, *N*-alkylpiperidines, and dimethylformamide to give dehydrohalogenation and halogen substitution products whose ratio depended on the reagent structure. Heating of 2-(1-iodoethyl)-3,5-dimethyl-1-methylsulfonyl-2,3-dihydro-1*H*-indole with piperidine resulted in the formation of only dehydroiodination products.

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Vinylindole derivatives attract researchers' attention as starting materials for the synthesis of a number of heterocyclic compounds. Apart from functionalization at the olefinic fragment, vinylindoles are used in the synthesis of carbazole derivatives with different degrees of hydrogenation [2–4], pyrrolo[1,2-*a*]indoles [5, 6], and tetracyclic core of lundurine alkaloids exhibiting antitumor activity [7].

2,3-Dihydroindoles having a vinyl fragment in the 2-position are generally obtained by cyclization of *o*-allylaniline in the presence of metal complex catalysts on the basis of mercury or palladium salts [8–10] or organotin compounds [7].

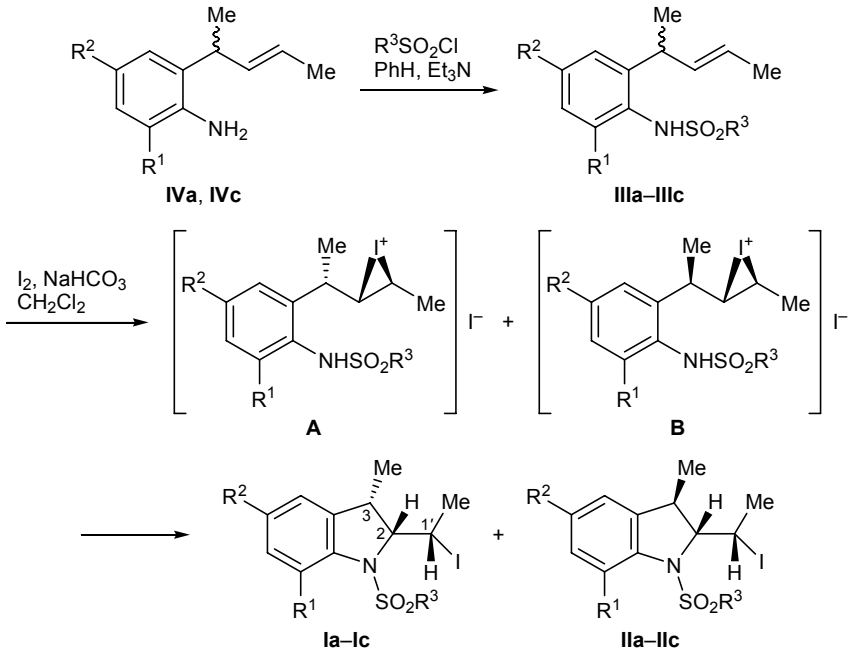
In the present article we describe the synthesis of 2-vinylindole derivatives from iodocyclization products **I** and **II**. The $C^{1'}$, C^2, and C^3 atoms in the resulting dihydroindoles were assigned (*S**)- or (*R**)-configuration on the basis of the assumed iodocyclization mechanism which implies formation of iodonium intermediates **A** or **B** with different orientations of the methyl group on $C^{1'}$. Intramolecular nucleophilic (S_N2) attack by the nitrogen atom on $C^{2'}$ in **A** and **B** leads to stereoisomeric dihydroindoles **I** and **II** differing by configuration of C^3 (Scheme 1).

trans Isomer **IIa** was formed as the major product, and it can readily be separated from *cis* isomer **Ia** by recrystallization from ethanol. *cis* Isomer **Ia** was isolated from the mother liquor by chromatography on silica gel; it was a viscous material containing up to 10% of unidentified impurity. *trans* Isomer **IIb** also predominated among the cyclization products obtained from *o*-nitrobenzenesulfonyl analog **IIIb**; however, we failed to separate it from *cis* isomer **Ib** by crystallization from ethanol. Therefore, coupling constants for the 2-H, 3-H, and 1′-H protons and methyl protons in minor isomer **Ib** were determined from the ^{1}H NMR spectrum of isomer mixture enriched in that isomer. Isomeric dihydroindoles **Ic** and **IIc** were separated by chromatography on silica gel.

Heating of *trans* isomer **IIa** in boiling piperidine resulted in the formation of a mixture of dehydroiodination products **V** and **VI** and halogen substitution product **VII** (see table) in an overall yield of 78%. Compound **VII** was converted into hydrochloride **VIII** by treatment with a solution of HCl; hydrochloride **VIII** is readily soluble in methylene chloride and ethanol but sparingly soluble in water, so that it can be isolated together with heterocycles **V** and **VI**. The latter crystallized from a solution in ethanol on cooling, while hydrochloride **VIII** remained in the filtrate (Scheme 2). After removal of the solvent, hydrochloride **VIII** containing small impurities of compounds **V** and **VI** was dissolved in methylene chloride, and the solution was treated with a saturated solution of $NaHCO_3$ to precipitate base **VII** containing 4% of **V** and **VI**. Recrystallization gave analytically pure compound **VII**, and pure hydrochloride **VIII** was isolated

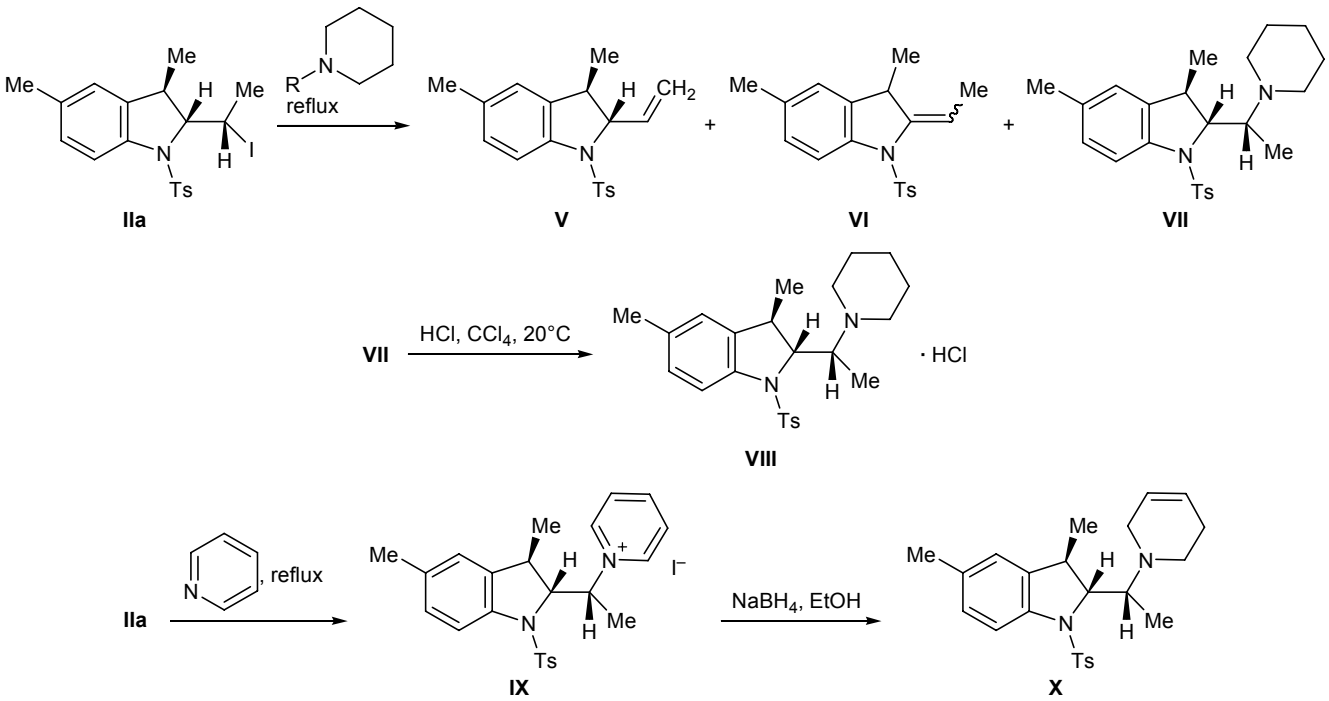
* For communication IX, see [1].

Scheme 1.



Ratio **Ia**/**IIa** 1 : 5, **Ib**/**IIb** 1 : 5, **Ic**/**IIc** 1 : 1;
R^1 = H, R^2 = Me, R^3 = 4-MeC_6H_4 (**a**), 2-$O_2NC_6H_4$ (**b**); R^1 = Me, R^2 = H, R^3 = 4-MeC_6H_4 (**c**).

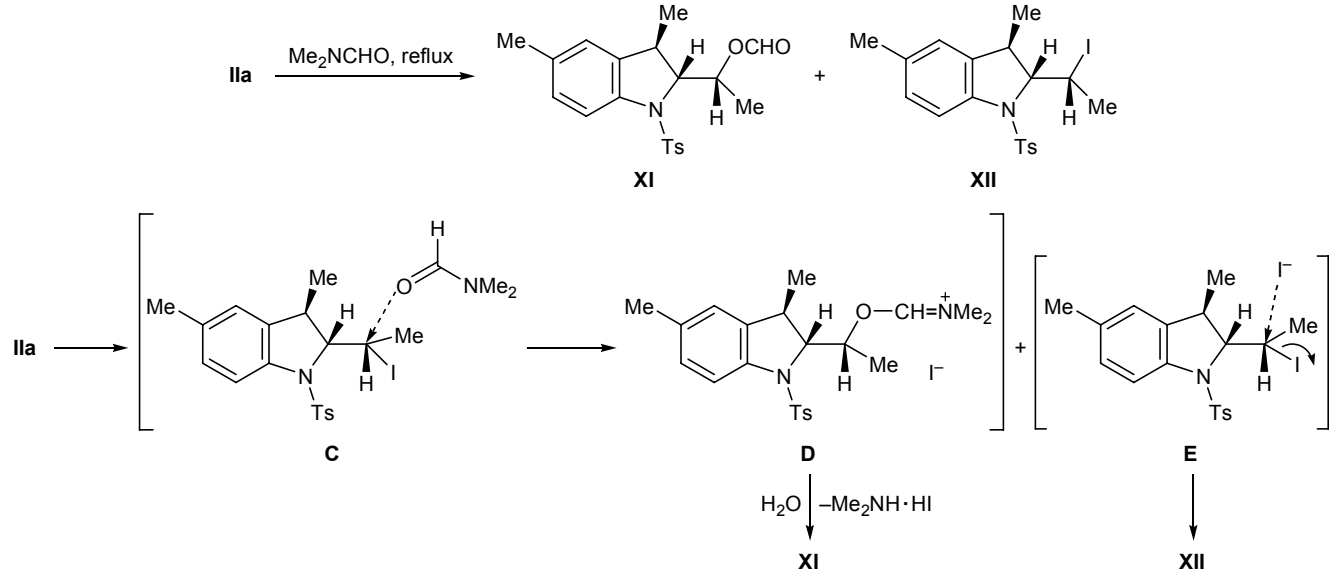
Scheme 2.



as a viscous material (yield 89%) by bubbling hydrogen chloride through a solution of **VII** in carbon tetrachloride. The presence of an ammonium fragment in molecule **VIII** impairs resolution of signals in the ^{1}H NMR spectrum up to transformation of doublets from methyl protons and signals from the aliphatic fragment into broadened singlets. The conjugate acid proton signal was observed at δ 12.2 ppm.

With a view to avoid formation of amine **VII**, compound **IIa** was heated in boiling *N*-methylpiperidine.

Scheme 3.



The reaction was complete in 30 h, and vinyl derivative **V** was isolated in 80% yield (after crystallization from ethanol), whereas no isomer **VI** was present. Analogous transformation of **IIa** in *N*-propylpiperidine required considerably shorter time, the yield of dehydrohalogenation product **V** being approximately the same (see table).

No appreciable dehydroiodination occurred when compound **IIa** was heated in triethylamine or diisopropylamine over a period of 5 h, and the initial compound was recovered almost completely. Despite strong basicity of these amines, their boiling point is likely to be insufficiently high to ensure dehydrohalogenation of **IIa**. Dehydrohalogenation of **IIa** with a less basic amine (pyridine; pK_a of the conjugate acid is 5.2) also produced a small amount of *N*-tosyl derivative **V**, while the major product was quaternary salt **IX**. The fraction of 2-vinyldihydroindole **V** did not exceed 12%. The reduction of pyridinium salt **IX** with sodium tetrahydridoborate gave compound **X**.

Reaction of compound **IIa** with amines

Amine	Reaction conditions	Yield, %		
		V	**VI**	**VIII**
Triethylamine	89°C, 5 h	–	–	–
Diisopropylamine	84°C, 5 h	–	–	–
Piperidine	106°C, 5 h	60	20	20
N-Methylpiperidine	108°C, 30 h	80	–	–
N-Propylpiperidine	152°C, 4 h	76	–	–

When compound **IIa** was heated in boiling DMF, only halogen substitution product was formed, whereas dehydrohalogenation products were not detected. Chromatographic separation of the product mixture on silica gel gave formic acid ester **XI** and (assumingly) (1′*R**)-isomer **XII** (~20%; Scheme 3). Presumably, ester **XI** is formed following the reaction sequence **IIa**→**C**→**D** which includes replacement of the halogen atom by quaternary salt fragment and hydrolysis to ester **XI**. Compound **XII** is likely to result from S_N2 reaction of iodide ion at the $C^{1'}$ atom of initial compound **IIa**. Factors responsible for higher stability of the isomer with reversed configuration of substituents on $C^{1'}$ at high temperature were not clarified.

In order to estimate the effect of the size of the substituent on the nitrogen atom on the possibility for formation of 2-ethylidenedihydroindole, *N*-mesyl derivative **XIII** was heated in boiling piperidine [11]. As a result, a mixture of 2-vinyldihydroindole **XIV**, 2-ethylidenedihydroindole **XV**, and 2-ethylindole **XVI** was obtained (overall yield 90%). According to the ^{1}H NMR data, the isomer ratio was ~1 : 1 : 1. The reaction mixture was a viscous material which failed to crystallize. Ethylidene derivative **XV** was likely to undergo isomerization into 2-ethylindole **XVI** during chromatography (the fraction of **XVI** considerably increased). Compound **XIV** was isolated in 17% yield. The remaining part of the product isolated by chromatography was 2-ethylindole **XVI** (48%). Obviously, 2-ethylindole **XVI** can be formed only from ethylidene derivative **XV** via 1,3-H shift from C^3 to $C^{1'}$. Fairly high yield of indole **XVI** indicates that compound **XIII**

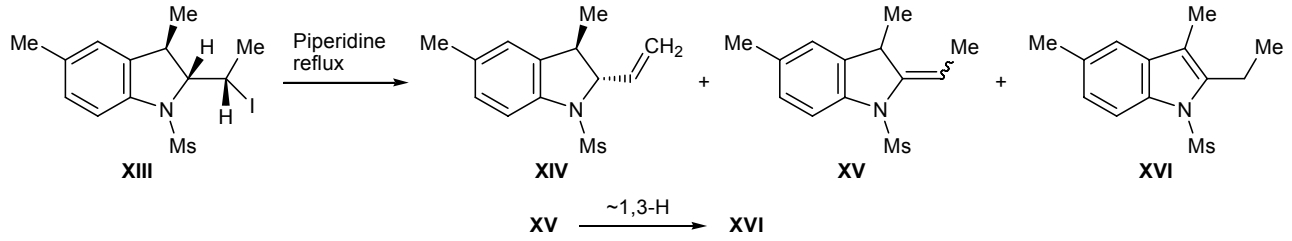
having a relatively small substituent on the nitrogen atom preferentially undergoes Zaitsev elimination and that compound **IIa** reacts according to Hofmann (Scheme 4).

As initial compound for the synthesis of 2-vinyldihydroindole we used *N*-(2-nitrophenylsulfonyl) derivative **IIb**. The product mixture obtained by heating compound **IIb** in boiling piperidine was subjected to vacuum distillation. Two fractions were collected. The first fraction (bp < 120°C) contained target product **XVIII** in a mixture with **XVII** and **XX**. The second fraction (bp 120–125°C) consisted mainly of compound **XVII** with small impurities of **XVIII** and **XX**. After chromatography, the overall yield of **XVIII** was 5%. The still residue was likely to contain mainly halogen replacement product **XIX**. Presumably, isomerization of initially formed ethylidene precursor **XXI** leads to indole **XX** (Scheme 5).

The structure of the synthesized compounds was determined on the basis of their elemental compositions and spectral data. Mutual orientation of substituents at C^2 and C^3 in compounds **Ia**–**Ic** and **IIa**–**IIc** was assigned taking into account published data [12]. The 3-H signal in the ^{1}H NMR spectra of **IIa** (δ 3.05 ppm, d.q, J = 3.5, 7.0 Hz), **IIb** (δ 3.15 ppm, d.q, J = 2.5, 7.0 Hz), and **IIc** (δ 2.85 ppm, d.q, J = 2.2, 7.1 Hz) appears in a weaker field relative to the corresponding signal of **Ia** (δ 2.78 ppm, d.q, J = 7.3, 8.2 Hz) and **Ic** (δ 2.55 ppm, quint, J = 7.6 Hz) (Fig. 1). Compound **Ib** does not fit the above relation; the chemical shift of 3-H in **Ib** is similar to that of 3-H in *trans* isomer **IIb**. Nevertheless, the coupling constants of 2-H with 3-H in *cis* isomers **Ia** (δ 4.63 ppm, $J_{2,1'}$ = 4.7, $J_{2,3}$ = 8.2 Hz), **Ib** (δ 4.43 ppm, $J_{2,1'}$ = 4.0, $J_{2,3}$ = 8.1), and **Ic** (δ 4.68 ppm, $J_{2,1'}$ = 4.4, $J_{2,3}$ = 7.6 Hz) are fairly large, indicating *cis* orientation of these protons with respect to each other. On the other hand, small coupling constants of 2-H in **IIa** (δ 3.41 ppm, J = 3.5, 7.2 Hz), **IIb** (δ 3.77 ppm, J = 2.5, 5.0 Hz), and **IIc** (δ 3.70 ppm, J = 2.2, 8.2 Hz) with 3-H ($J_{2,3}$ = 3.5, 2.5, and 2.2 Hz, respectively) are typical of their *trans* arrangement. The 1′-H proton in the ethyl fragment of *cis* isomers **Ia** (δ 4.39 ppm, $J_{1',2}$ = 4.7, $J_{1',Me}$ = 7.1 Hz), **Ib** (δ 4.62 ppm, J = 4.0, 7.2 Hz), and **Ic** (δ 4.28 ppm (J = 4.4, 6.9 Hz) resonates as a doublet of quartets. The corresponding signal of *trans* isomer **IIa** is a quintet (δ 4.47 ppm, J = 7.2 Hz), while the 1′-H signals of **IIc** (δ 4.09 ppm, J = 7.1, 8.2 Hz) (Fig. 2) and **IIb** (δ 4.49 ppm, J = 5.0, 7.2 Hz) are doublets of quartets.

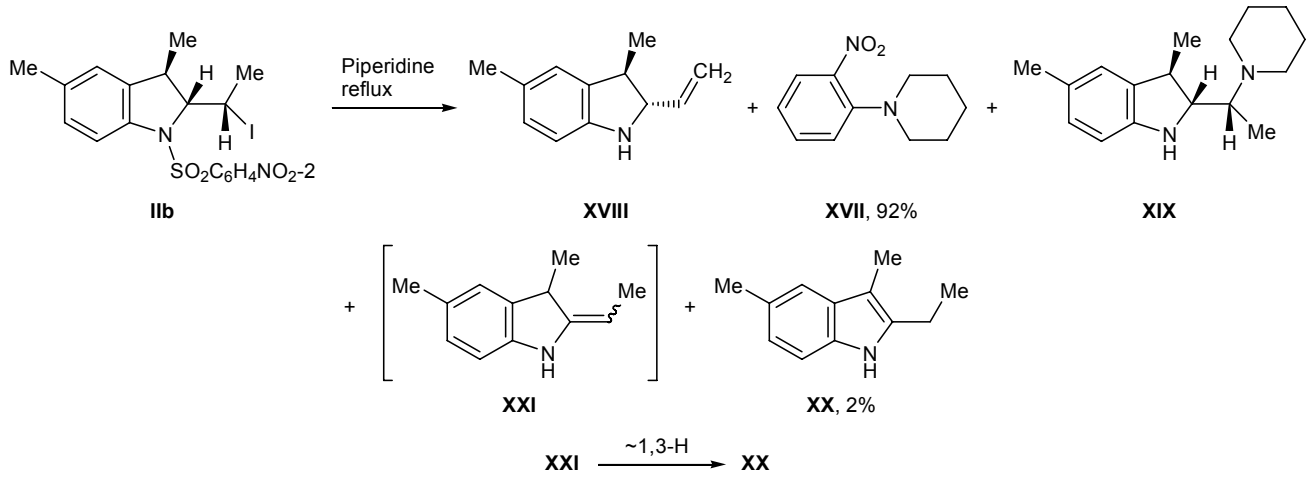
Protons in the methyl group on C^3 in *cis* isomers **Ia**–**Ic** give rise to a doublet at δ 1.30–1.45 ppm, and methyl protons in the iodoethyl fragment resonate at δ

Scheme 4.



XIII **XIV** **XV** **XVI**

Scheme 5.



IIb **XVIII** **XVII**, 92% **XIX**

XXI **XX**, 2%

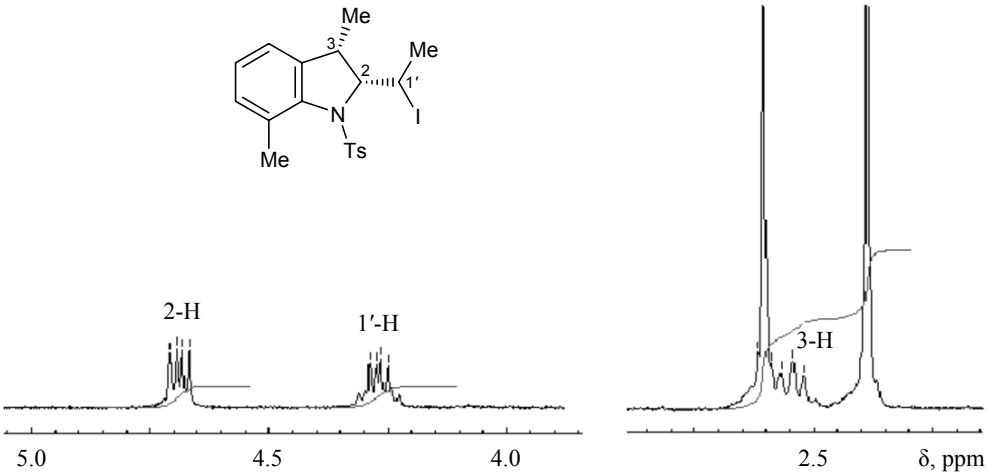


Fig. 1. A fragment of the ^{1}H NMR spectrum of compound **Ic** corresponding to resonances of the 1′-H, 2-H, and 3-H protons.

1.55–1.80 ppm. The difference in the chemical shifts of these methyl protons reaches 0.5 ppm. In going from *cis* orientation of the 3-Me group and 1-iodoethyl group on C^2 to *trans* (**IIa**–**IIc**) the difference in the chemical shifts of the methyl protons increased to 1.50 ppm. The C**H**$_3$CHI signal of **IIa** (δ 0.60 ppm, J = 7.0 Hz), **IIb** (δ 0.85 ppm, J = 7.2 Hz), and **IIc** (δ 0.50 ppm, J = 7.1 Hz) appeared in a stronger field, while the 3-Me signal of **IIa** (δ 2.00 ppm, J = 7.2 Hz), **IIb** (δ 1.98 ppm, J = 7.0 Hz), and **IIc** (δ 2.05 ppm, J = 7.1 Hz) was displaced downfield.

Comparison of the ^{1}H NMR spectra of **IIa** and **XIII** showed that the chemical shift of 3-H depends to some extent on the substituent on the nitrogen atom. The 3-H signal of **IIa** was located in a stronger field (δΔ ≈ 0.3 ppm) relative to the 3-H signal of **XIII** [11]. Compounds **IIa** and **XIII** are characterized by different multiplicities of the 1′-H signal; the latter appears as a quintet at δ 4.47 ppm ($J_{2,1'}$ = 7.2 Hz) in the ^{1}H NMR spectrum of **IIa** but as a doublet of quartets in the spectrum of *N*-mesyl analog **XIII** [11].

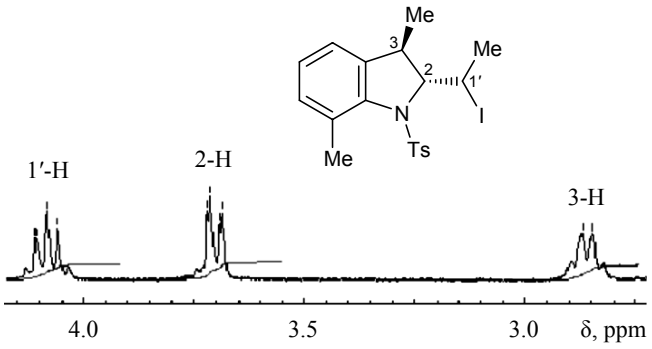


Fig. 2. A fragment of the ^{1}H NMR spectrum of compound **IIc** corresponding to resonances of the 1′-H, 2-H, and 3-H protons.

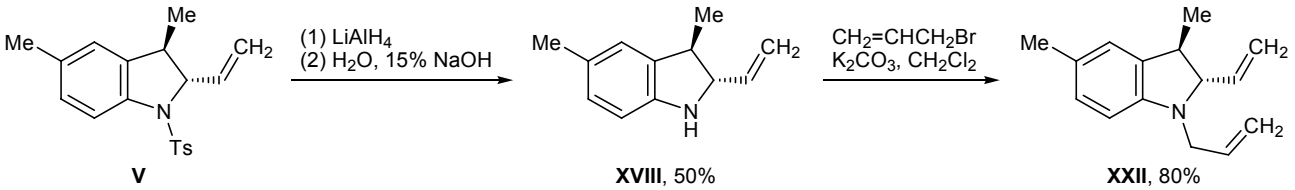
The vinyl group in dihydroindoles **V** and **XIV** gives rise to characteristic signals from protons in the terminal methylene group with a small geminal coupling constant (J = 1.0 Hz); the vicinal coupling constants with 1′-H are J_{cis} = 10.2–10.3 and J_{trans} = 16.9–17.6 Hz. Ethylidene derivative **VI** was identified in a mixture with compound **V** by the presence of a quartet signal from 1′-H at δ ~6 ppm.

The mass spectrum of **XI** (positive ion detection) contained the molecular ion peak with m/z 374 $[M + H]^+$. The negative ion mass spectrum was less informative. The most abundant ion therein was toluenesulfonyl fragment, m/z 155 $[CH_3C_6H_4SO_2]^-$.

Ester **XI** displayed fairly characteristic signals from the formate group in the ^{1}H and ^{13}C NMR spectra. The OCHO signal appeared in the ^{1}H NMR spectrum of **XI** as a singlet at δ 7.80 ppm, and the carbonyl carbon atom gave rise to a doublet at δ_C 159.5 ppm in the JMOD ^{13}C NMR spectrum.

Comparison of the NMR spectra of compound **XII** (the assumed product of inversion of configuration at $C^{1'}$) and isomers **Ia** and **IIa** showed that the CHIC**H**$_3$ signal of **XII** (δ 0.50 ppm), as well as of **IIa**, is located in a stronger field than the corresponding signal of stereoisomer **Ia** (Δδ ~0.85 ppm). The positions of other signals in the ^{1}H NMR spectra of these compounds are also considerably different. Isomerization with formation of 3-iodo-1,2,3,4-tetrahydroquinoline derivative was ruled out on the basis of the calculation data, according to which the chemical shift of C^2 neighboring to the nitrogen atom in dihydroindole derivatives is about δ_C 75 ppm, whereas C^2 in quinoline derivatives resonates at δ_C ~60 ppm. In addition, the methyl carbon signal of the iodoethyl group in the ^{13}C NMR

Scheme 6.



spectrum of **XII** was displaced appreciably downfield (δ_C 30.6 ppm) due to the presence of heavy iodine atom at the neighboring carbon atom (cf. δ_C 34.1 ppm for isomer **IIa**).

The ^{1}H NMR spectrum of compound **XVIII** obtained from dihydroindole derivatives **IIb** and **V** retained signal splitting pattern characteristic of the terminal methylene group.

The reduction of tosyl derivative **V** with excess lithium tetrahydridoaluminate afforded 50% of **XVIII**, i.e., the yield was slightly higher than in the reaction of nitrobenzenesulfonyl derivative **IIb** with piperidine. The subsequent treatment of the reaction mixture with water to neutralize large excess of the reducing agent is a fairly long and unsafe process, for the reaction is rather vigorous. The alkylation of **XVIII** with allyl bromide gave *N*-allyl derivative **XXII** (Scheme 6).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. 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 mass spectrum (atmospheric pressure chemical ionization) was obtained on a Shimadzu 2010EV LC–MS instrument using methanol–water (1 : 1) as eluent. The elemental compositions were determined on a Hewlett–Packard M-185B CHN analyzer. Silica gel LS (40–100 μm, Lancaster) was used for column chromatography. Qualitative TLC analyses were performed using Sorbfil plates (*Sorbpolimer* close corporation, Krasnodar, Russia); spots were developed by treatment with iodine vapor.

(2*R,3*R**)-2-[(1*S**)-1-Iodoethyl]-3,5-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole (IIa).** A mixture of 4.93 g (15 mmol) of *p*-toluenesulfonamide (**IIIa**), 8.10 g (96 mmol) of sodium hydrogen carbonate, and 7.62 g (30 mmol) of iodine in 200 ml of methylene chloride was stirred for ~24 h at 20°C, the progress of the reaction being monitored by TLC (eluent CH_2Cl_2). When the reaction was complete, the mixture was diluted with 500 ml of methylene chloride, 200 ml of water was added, the mixture was stirred for 5 min, and the organic phase was treated with a 10% solution of $Na_2S_2O_3$ (3×100 ml) and water (200 ml), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was treated with 100 ml of ethanol, the mixture was stirred, and the precipitate was filtered off and recrystallized from ethanol (200 ml). Yield 2.86 g (42%), mp 169°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.60 d (3H, CH_3, J = 7.0 Hz), 2.00 d (3H, CH_3, J = 7.2 Hz), 2.31 s (3H, CH_3), 2.37 s (3H, CH_3), 3.05 d.q (1H, 3-H, J = 3.5, 7.0 Hz), 3.41 d.d (1H, 2-H, J = 3.5, 7.2 Hz), 4.47 quint (1H, 1′-H, J = 7.2 Hz), 6.82 s (1H, 4-H), 7.04 d (1H, H_{arom}, J = 8.0 Hz), 7.17 d (2H, H_{arom}, J = 8.3 Hz), 7.50 d (2H, H_{arom}, J = 8.3 Hz), 7.57 d (1H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.5, 21.8, 22.5, 34.1 (CH_3); 25.4 ($C^{1'}$), 43.1 (C^3), 75.4 (C^2); 117.6, 125.0, 127.9, 129.0, 129.4 (C^4, C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 134.3, 135.5, 136.9, 139.0, 143.4 (C^{3a}, C^5, C^{7a}, $C^{1'}$, $C^{4'}$). Found, %: C 50.01; H 4.81; I 27.78; N 2.98; S 6.95. $C_{19}H_{22}INO_2S$. Calculated, %: C 50.12; H 4.87; I 27.87; N 3.08; S 7.04.

The first alcoholic mother liquor was evaporated under reduced pressure at a bath temperature of no higher than 40°C, the dry residue was dissolved in a minimal amount of benzene (~10 ml), and the solution was applied to a column charged with silica gel (60 g). Elution with benzene gave (2*R**,3*S**)-2-[(1*S**)-1-iodoethyl]-3,5-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole (**Ia**) containing an unidentified impurity. R_f 0.6 (C_6H_6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.35 d (3H, CH_3, J = 7.3 Hz), 1.80 d (3H, CH_3, J = 7.1 Hz), 2.28 s (3H, CH_3), 2.36 s (3H, CH_3), 2.78 d.q (1H, 3-H, J = 7.3, 8.2 Hz), 4.39 d.q (1H, 1′-H, J = 4.7, 7.1 Hz), 4.63 d.d (1H, 2-H, J = 4.7, 8.2 Hz), 6.76 s (1H, 4-H), 7.09 d (1H, H_{arom}, J = 8.0 Hz), 7.17 d (2H, H_{arom}, J = 8.0 Hz), 7.53 d (2H, H_{arom}, J = 8.0 Hz), 7.58 d (1H, H_{arom}, J = 8.0 Hz).

(2*R,3*R**)-2-[(1*S**)-1-Iodoethyl]-3,5-dimethyl-1-(2-nitrophenylsulfonyl)-2,3-dihydro-1*H*-indole (IIb).** A mixture of 9.3 g (26 mmol) of 2-nitrobenzenesulfonamide (**IIIb**), 15.6 g (185 mmol) of sodium hydrogen carbonate, and 14.1 g (55 mmol) of iodine in

300 ml of methylene chloride was stirred for ~104 h at 20°C. The mixture was diluted with 500 ml of methylene chloride and filtered, and the precipitate was washed with 100 ml of methylene chloride. The organic phase was treated with a 10% solution of $Na_2S_2O_3$ (3×200 ml) and water (200 ml), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was stirred with 100 ml of ethanol, the mixture was stirred, and the precipitate was filtered off and recrystallized from ethanol (200 ml). However, we failed to isolate pure compound **IIb** by repeated crystallization from ethanol. It was isolated by column chromatography on silica gel using benzene as eluent. Yield 2.8 g (20%), mp 171–172°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 d (3H, CH_3, J = 7.2 Hz), 1.98 d (3H, CH_3, J = 7.0 Hz), 2.35 s (3H, CH_3), 3.15 d.q (1H, 3-H, J = 2.5, 7.0 Hz), 3.77 d.d (1H, 2-H, J = 2.5, 5.0 Hz), 4.49 d.q (1H, 1′-H, J = 5.0, 7.2 Hz), 6.91 s (1H, 4-H), 7.09 d.d (1H, H_{arom}, J = 1.0, 8.2 Hz), 7.44–7.68 m (5H, H_{arom}). Found, %: C 44.41; H 3.90; I 25.93; N 5.61; S 6.37. $C_{18}H_{19}IN_2O_4S$. Calculated, %: C 44.46; H 3.94; I 26.09; N 5.76; S 6.59.

A mixture of stereoisomers **Ic** and **IIc** was obtained as described above for **Ia**/**IIa** from 0.49 g (1.5 mmol) of *p*-toluenesulfonamide (**IIIc**). After appropriate treatment of the reaction mixture and removal of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel using benzene as eluent.

(2*R,3*S**)-2-[(1*S**)-1-Iodoethyl]-3,7-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole (Ic).** Yield 0.24 g (35%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 d (3H, CH_3, J = 7.6 Hz), 1.55 d (3H, CH_3, J = 6.9 Hz), 2.35 s (3H, CH_3), 2.62 s (3H, CH_3), 2.55 quint (1H, 3-H, J = 7.6 Hz), 4.28 d.q (1H, 1′-H, J = 4.4, 6.9 Hz), 4.68 d.d (1H, 2-H, J = 4.4, 7.6 Hz), 6.77 d (1H, H_{arom}, J = 6.6 Hz), 7.05–7.17 m (4H, H_{arom}), 7.45 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 49.99; H 4.81; I 27.82; N 3.03; S 6.98. $C_{19}H_{22}INO_2S$. Calculated, %: C 50.12; H 4.87; I 27.87; N 3.08; S 7.04.

(2*R,3*R**)-2-[(1*S**)-1-Iodoethyl]-3,7-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole (IIc)** was isolated by further elution. Yield 0.21 g (31%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.50 d (3H, CH_3, J = 7.1 Hz), 2.05 d (3H, CH_3, J = 7.1 Hz), 2.35 s (3H, CH_3), 2.62 s (3H, CH_3), 2.85 d.q (1H, 3-H, J = 2.2, 7.1 Hz), 3.70 d.d (1H, 2-H, J = 2.2, 8.2 Hz), 4.09 d.q (1H, 1′-H, J = 7.1, 8.2 Hz), 6.88 d (1H, H_{arom}, J = 6.8 Hz), 7.03–7.20 m (4H, H_{arom}), 7.36 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 49.96; H 4.80; I 27.79; N 3.04; S 6.97. $C_{19}H_{22}INO_2S$. Calculated, %: C 50.12; H 4.87; I 27.87; N 3.08; S 7.04.

4-Methyl-*N*-{4-methyl-2-[(2*E*)-1-methylbut-2-en-1-yl]phenyl}benzenesulfonamide (IIIa). 2-(1-Methylbut-2-en-1-yl)-4-methylaniline (**IVa**), 3.5 g (20 mmol), was dissolved in 20 ml of benzene, 4 ml of triethylamine and 4.18 g (22 mmol) of *p*-toluenesulfonyl chloride were added, and the mixture was left to stand for 24 h at 20°C. The mixture was treated with 10 ml of water, stirred for 30 min, and extracted with 60 ml of methylene chloride. The organic phase was washed with 10 ml of water, dried over $MgSO_4$, and evaporated under reduced pressure to isolate compound **IIIa** as a viscous oily substance.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

***N*-{4-Methyl-2-[(2*E*)-1-methylbut-2-en-1-yl]-phenyl}-2-nitrobenzenesulfonamide (IIIb)** was synthesized from 17.5 g (100 mmol) of pentenylaniline **IVb** and 26.6 g (120 mmol) of 2-nitrobenzenesulfonyl chloride. The product was isolated as a viscous material. Attempted crystallization from ethanol gave compound **IIIb** as an oily substance which was brought into iodocyclization.

4-Methyl-*N*-{2-methyl-6-[(2*E*)-1-methylbut-2-en-1-yl]phenyl}benzenesulfonamide (IIIc) was synthesized in a similar way from 1.75 g (10 mmol) of alkenylaniline **IVc** and 2.09 g (11 mmol) of *p*-toluenesulfonyl chloride. Viscous material crystallized upon addition of methanol. Yield 2.63 g (80%), mp 115°C (from EtOH). If that material was dissolved in hot ethanol, compound **IIIc** did not crystallize on cooling. Found, %: C 69.21; H 7.02; N 4.22; S 9.69. $C_{19}H_{23}NO_2S$. Calculated, %: C 69.27; H 7.04; N 4.25; S 9.73.

(2*S,3*R**)-3,5-Dimethyl-1-(4-methylphenylsulfonyl)-2-vinyl-2,3-dihydro-1*H*-indole (V).** A mixture of 0.455 g (1 mmol) of compound **IIa** and 6 ml of *N*-methylpiperidine or *N*-propylpiperidine was heated under reflux for 30 or 4 h, respectively. The solvent was removed under reduced pressure, the residue was dissolved in 50 ml of carbon tetrachloride, and the solution was treated with 30 ml of water by shaking in a separatory funnel. The organic phase was washed with 20 ml of 3% aqueous HCl and 20 ml of water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was dissolved in 5 ml of boiling ethanol; after cooling, the precipitate was filtered off. Yield 0.26 g (80%) (in *N*-methylpiperidine), 0.25 g

(76%) (in *N*-propylpiperidine); mp 141–142°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.70 d (3H, CH_3, J = 7.0 Hz), 2.25 s (3H, CH_3), 2.40 s (3H, CH_3), 2.85 d.q (1H, 3-H, J = 4.3, 7.0 Hz), 4.07 d.d.t (1H, 2-H, J = 1.0, 4.3, 6.7 Hz), 5.15 d.t (2′-H, J = 1.0, 10.3 Hz), 5.38 d.t (1H, 2′-H, J = 1.0, 16.9 Hz), 5.95 d.d.d (1H, 1′-H, J = 6.7, 10.3, 16.9 Hz), 6.80 s (1H, 4-H), 7.02 d (1H, H_{arom}, J = 7.4 Hz), 7.22 d (2H, H_{arom}, J = 8.0 Hz), 7.51 d (1H, H_{arom}, J = 7.4 Hz), 7.60 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 69.47; H 6.25; N 4.04; S 9.58. $C_{19}H_{21}NO_2S$. Calculated, %: C 69.69; H 6.46; N 4.28; S 9.79.

(2*R,3*R**)-3,5-Dimethyl-1-(4-methylphenylsulfonyl)-2-[(1*R**)-1-(piperidin-1-yl)ethyl]-2,3-dihydro-1*H*-indole (VII).** A solution of 1.9 g (4.17 mmol) of compound **IIa** in 20 ml of piperidine was heated for 4 h under reflux. Piperidine was removed under reduced pressure, the residue was dissolved in 200 ml of methylene chloride, the solution was washed with water (3×30 ml), treated with 5% aqueous HCl (30 ml) under shaking, washed with water (30 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure (water-jet pump), and the residue was crystallized from ethanol (10 ml). Crystals of 2-vinyl and 2-ethylidene derivatives **V** and **VI** were filtered off. Yield 0.92 g (68%), ratio **V**:**VI** = 3:1.

The mother liquor was evaporated under reduced pressure, the residue was dissolved in 100 ml of methylene chloride, and the solution was washed with a saturated solution of sodium hydrogen carbonate until carbon dioxide no longer evolved and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was dissolved in boiling ethanol. After cooling, the powder-like precipitate (0.27 g) was filtered off; it was compound **VII** containing ~3% of **V** and ~1% of **VI** as impurities. Compound **VII** was purified by repeated recrystallization from ethanol, mp 169–170°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.48 d (3H, CH_3, J = 7.0 Hz), 0.80 d (3H, CH_3, J = 6.8 Hz), 1.30–1.60 m (6H, CH_2), 2.20 s (3H, CH_3), 2.30 s (3H, CH_3), 2.49–2.60 m (4H, CH_2), 2.85 d.q (1H, 1′-H, J = 3.0, 7.0 Hz), 3.00 d.q (1H, 3-H, J = 2.0, 6.8 Hz), 3.84 m (1H, 2-H), 6.69 s (4-H), 6.90 d (1H, H_{arom}, J = 8.0 Hz), 7.12 d (2H, H_{arom}, J = 8.0 Hz), 7.48 d (1H, H_{arom}, J = 8.0 Hz), 7.52 d (2H, H_{arom}, J = 8.0 Hz).

(2*R,3*R**)-3,5-Dimethyl-1-(4-methylphenylsulfonyl)-2-[(1*R**)-1-(piperidin-1-yl)ethyl]-2,3-dihydro-1*H*-indole hydrochloride (VIII).** Compound **VII**, 0.11 g (0.25 mmol), containing a small impurity of **V** and **VI** was dissolved in 10 ml of carbon tetrachloride, and gaseous HCl was bubbled through the solution. After a few minutes, the solution turned turbid, but then rapidly clarified. Bubbling of HCl was continued for 10 min more, and viscous hydrochloride **VIII** deposited on the walls of the reaction test tube. The organic phase was removed by decanting, and hydrochloride **VIII** remaining on the walls was dried under reduced pressure. Yield 0.1 g (89%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.60 br.s (3H, CH_3), 1.30–1.60 m (6H, CH_2), 1.30 s (3H, CH_3), 2.25 s (3H, CH_3), 2.40 s (3H, CH_3), 3.00 m (1H, 3-H), 3.10 m (1H, 2-H), 3.40–3.70 m (4H, CH_2), 3.80 m (1H, 1′-H), 6.88 s (4-H), 7.04 d (1H, H_{arom}, J = 8.3 Hz), 7.22 d (2H, H_{arom}, J = 8.2 Hz), 7.53 d (1H, H_{arom}, J = 8.3 Hz), 7.59 d (2H, H_{arom}, J = 8.2 Hz), 12.2 br.s (HCl). Found, %: C 63.98; H 7.29; Cl 7.87; N 6.05; S 6.96. $C_{24}H_{33}ClN_2O_2S$. Calculated, %: C 64.19; H 7.41; Cl 7.90; N 6.24; S 7.14.

1-[(1*R)-1-{(2*R**,3*R**)-3,5-Dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indol-2-yl}ethyl]-pyridinium iodide (IX).** A mixture of 0.6 g (1.32 mmol) of compound **IIa** and 40 ml of pyridine was heated for 24 h under reflux. Excess pyridine was removed under reduced pressure, the solid residue was treated with 10 ml of water, and the mixture was thoroughly stirred and extracted with chloroform. The organic phase was washed with water (2×80 ml), dried over $MgSO_4$, filtered from the drying agent, and evaporated under reduced pressure. The residue was treated with 20 ml of carbon tetrachloride, the mixture was thoroughly stirred on heating under reflux for a few minutes, and the undissolved brown quaternary salt was filtered off. Yield 0.5 g (71%), mp 294–295°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.46 d (3H, CH_3, J = 7.2 Hz), 2.09 d (3H, CH_3, J = 6.8 Hz), 2.19 s (3H, CH_3), 2.26 s (3H, CH_3), 3.12 d.q (1H, 3-H, J = 1.0 6.8 Hz), 4.29 d.d (1H, 2-H, J = 1.0, 7.2 Hz), 4.93 quint (1H, 1′-H, J = 7.2 Hz), 6.75 s (1H, 4-H), 6.98 d (1H, H_{arom}, J = 7.8 Hz), 7.11 d (2H, H_{arom}, J = 8.3 Hz), 7.43 d (1H, H_{arom}, J = 7.8 Hz), 7.46 d (2H, H_{arom}, J = 8.3 Hz), 7.97 d.d (2H, H_{arom}, J = 5.8, 7.7 Hz), 8.37 t (1H, H_{arom}, J = 7.7 Hz), 9.22 d (2H, H_{arom}, J = 5.8 Hz). Found, %: C 53.76; H 4.87; I 23.43; N 5.02; S 5.81. $C_{24}H_{27}IN_2O_2S$. Calculated, %: C 53.94; H 5.09; I 23.74; N 5.24; S 6.00.

The residue obtained after evaporation of CCl_4 was recrystallized from ethanol to isolate 0.12 g of a mixture of approximately equal amounts of **V** and **IX**.

(2*R,3*R**)-2-{(1*R**)-1-[3,6-Dihydropyridin-1(2*H*)-yl]ethyl}-3,5-dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indole (X)** was synthesized by

reduction of 0.422 g (0.79 mmol) of **IX** with 0.121 g (3.16 mmol) of sodium tetrahydridoborate in 5 ml of anhydrous ethanol. When the reaction was complete, the mixture was diluted with water and extracted with 30 ml of methylene chloride. The extract was washed with 10 ml of water, dried over $MgSO_4$, and evaporated, and the residue was crystallized from ethanol, mp 153–154°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.51 d (3H, CH_3, J = 7.1 Hz), 0.91 d (3H, CH_3, J = 6.8 Hz), 2.07–2.11 m (2H, CH_2), 2.26 s (3H, CH_3), 2.34 s (3H, CH_3), 2.61–2.85 m (2H, CH_2), 2.91–3.20 m (4H, CH_2, 3-H, 1′-H), 3.97 d.d (1H, 2-H, J = 2.6, 3.5 Hz), 5.62–5.78 m (2H, CH=CH), 6.76 s (1H, 4-H), 6.98 d (1H, H_{arom}, J = 8.0 Hz), 7.17 d (2H, H_{arom}, J = 8.0 Hz), 7.55 d (1H, H_{arom}, J = 8.0 Hz), 7.58 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 70.14; H 7.31; N 6.77; S 7.74. $C_{24}H_{30}N_2O_2S$. Calculated, %: C 70.21; H 7.36; N 6.82; S 7.81.

(1*R)-1-{(2*R**,3*R**)-3,5-Dimethyl-1-(4-methylphenylsulfonyl)-2,3-dihydro-1*H*-indol-2-yl}ethyl formate (XI).** A solution of 0.455 g (1 mmol) of compound **IIa** in 5 ml of DMF was heated for 2 h under reflux. The solvent was removed under reduced pressure, 50 ml of methylene chloride and 30 ml of water were added to the residue, the mixture was shaken in a separatory funnel, and the organic layer was separated, washed with water (20 ml), and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography using benzene as eluent. Yield 0.16 g (43%). Colorless powder, mp 145°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.45 d (3H, CH_3, J = 7.1 Hz), 1.08 d (3H, CH_3, J = 6.5 Hz), 2.15 s (3H, CH_3), 2.20 s (3H, CH_3), 2.85 d.q (1H, 3-H, J = 2.6, 6.5 Hz), 3.70 d.d (1H, 2-H, J = 2.6, 4.4 Hz), 5.25 m (1H, 1′-H), 6.60 s (1H, 4-H), 6.89 d (1H, H_{arom}, J = 8.0 Hz), 7.00 d (2H, H_{arom}, J = 8.0 Hz), 7.45 d (2H, H_{arom}, J = 8.0 Hz), 7.50 d (1H, H_{arom}, J = 8.0 Hz), 7.80 s (1H, OCHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.1, 21.1, 21.5, 22.6 (CH_3); 36.8 (C^3), 70.1 (C^2), 72.0 ($C^{1'}$); 116.7, 124.5, 127.4, 128.8, 129.4 (C^4, C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 134.2, 134.4, 137.1, 139.1, 143.6 (C^{3a}, C^5, C^{7a}, $C^{1'}$, C^4); 159.5 (OCHO). Mass spectrum, m/z: 374 $[M + H]^+$, 155 $[CH_3C_6H_4SO_2]^-$. Found, %: C 64.09; H 6.03; N 3.59; S 8.31. $C_{20}H_{23}NO_4S$. Calculated, %: C 64.32; H 6.21; N 3.75; S 8.58.

Further elution gave (2*R**,3*R**,1′*R**)-isomer **XII**. Yield 0.09 g (20%), colorless powder, mp 177°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.50 d (3H, CH_3, J = 6.9 Hz), 1.43 d (3H, CH_3, J = 6.9 Hz), 2.15 s (3H, CH_3), 2.20 s (3H, CH_3), 2.93 d.q (1H, 3-H, J = 2.5, 6.9 Hz), 3.70 d.d (1H, 2-H, J = 2.5, 3.8 Hz), 4.55 d.q (1H, 1′-H, J = 3.8, 6.9 Hz), 6.60 s (1H, 4-H), 6.85 d (1H, H_{arom}, J = 8.0 Hz), 6.99 d (2H, H_{arom}, J = 8.2 Hz), 7.41 d (2H, H_{arom}, J = 8.2 Hz), 7.44 d (1H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.1, 21.4, 21.8, 30.6 (CH_3); 24.4 ($C^{1'}$), 38.4 (C^3), 74.3 (C^2); 116.2, 124.8, 127.6, 129.1, 129.4 (C^4, C^6, C^7, $C^{2'}$, $C^{6'}$, $C^{3'}$, $C^{5'}$); 134.2, 135.1, 136.6, 139.9, 143.5 (C^{3a}, C^5, C^{7a}, $C^{1'}$, C^4). Found, %: C 50.03; H 4.78; I 27.75; N 3.04; S 6.97. $C_{19}H_{22}INO_2S$. Calculated, %: C 50.12; H 4.87; I 27.87; N 3.08; S 7.04.

(2*S,3*R**)-3,5-Dimethyl-1-methylsulfonyl-2-vinyl-2,3-dihydro-1*H*-indole (XIV).** A mixture of 1.9 g (5.01 mmol) of compound **XIII** and 20 ml of piperidine was heated for 5 h under reflux. The solvent was removed under reduced pressure, the residue was dissolved in 50 ml of methylene chloride, the solution was treated with 30 ml of water, and the mixture was shaken in a separatory funnel. The organic phase was separated, washed with 3% aqueous HCl (20 ml) on shaking and water (20 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel using benzene as eluent to isolate (in order of elution) 0.6 g (48%) of indole **XVI** and 0.217 g (17%) of 2-vinyl derivative **XIV** as a viscous material, R_f 0.2 (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.35 d (3H, CH_3, J = 7.0 Hz), 2.30 s (3H, CH_3), 2.90 s (3H, CH_3), 3.05 d.q (1H, 3-H, J = 4.4, 7.0 Hz), 4.27 d.d.d (1H, 2-H, J = 1.0, 4.4, 7.3 Hz), 5.17 d.t (2′-H, J = 1.0, 10.2 Hz), 5.38 d.t (1H, 2′-H, J = 1.0, 17.6 Hz), 5.95 d.d.d (1H, 1′-H, J = 7.3, 10.2, 17.6 Hz), 6.95 s (1H, 4-H), 7.02 d (1H, H_{arom}, J = 9.0 Hz), 7.30 d (1H, H_{arom}, J = 9.0 Hz). Found, %: C 61.97; H 6.55; N 5.34; S 12.51. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.82; N 5.57; S 12.76.

2-Ethyl-3,5-dimethyl-1-methylsulfonyl-1*H*-indole (XVI). Yield 0.6 g (48%), viscous transparent material, R_f 0.5 (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 t (3H, CH_3, J = 7.4 Hz), 2.20 s (3H, CH_3), 2.40 s (3H, CH_3), 2.85 s (3H, CH_3), 2.95 q (2H, 1′-H, J = 7.4 Hz), 7.12 d (1H, H_{arom}, J = 1.3, 8.4 Hz), 7.27 s (1H, 4-H), 7.89 d (1H, H_{arom}, J = 8.4 Hz). Found, %: C 61.94; H 6.57; N 5.30; S 12.48. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.82; N 5.57; S 12.76.

1-(2-Nitrophenyl)piperidine (XVII). Yield 9.56 g (92%), bp 125–128°C (2 mm). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.8 (C^4), 25.8 (C^3, C^5), 52.8 (C^2, C^6); 120.4, 120.7, 125.8, 133.2 (C_{arom}), 133.3 ($C^{1'}$), 146.9 ($C^{2'}$). Mass spectrum: m/z 207 $[M + H]^+$.

(2*S,3*R**)-3,5-Dimethyl-2-vinyl-2,3-dihydro-1*H*-indole (XVIII).** *a*. A solution of 0.27 g (0.6 mmol) of compound **V** in 20 ml of THF was added to a cold suspension of 0.456 g (12 mmol) of $LiAlH_4$ in 40 ml of THF. The mixture was stirred for 48 h at room temperature and cooled to 0°C, and 1.2 ml of water was added dropwise. Vigorous evolution of hydrogen was observed after addition of every drop of water. A 15% solution of sodium hydroxide, 1.2 ml, and water, 3.6 ml, were then added. The resulting suspension consisting of small granules was filtered, the solid material was washed with THF on a filter, the filtrate and the washings were evaporated, and the residue was subjected to column chromatography using benzene as eluent. Yield 0.05 g (50%).

b. A solution of 24.3 g (50 mmol) of compound **IIb** in 160 ml of piperidine was heated for 6 h under reflux. The solvent was removed under reduced pressure, the residue was dissolved in 250 ml of methylene chloride, the solution was treated in a separatory funnel with a saturated solution of sodium hydrogen carbonate until carbon dioxide no longer evolved, and the organic phase was separated, washed with water (70 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure (water-jet pump), and the residue was subjected to fractional distillation in a vacuum (oil pump). A fraction with bp 112–120°C (2 mm) was collected; it was a mixture of approximately equal amounts of compounds **XVIII** and **XX** and a small amount of 1-(2-nitrophenyl)piperidine (**XVII**). By column chromatography using benzene as eluent we isolated (from first fractions) 0.35 g (2%) of **XVIII** as a brown liquid. IR spectrum: ν 3385 cm^{-1} (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 d (3H, CH_3, J = 7.5 Hz), 2.25 s (3H, CH_3), 2.95 d.q (1H, 3-H, J = 6.7, 7.5 Hz), 3.80 d.d (1H, 2-H, J = 6.7, 7.5 Hz), 6.00 d.d.d (1H, 1′-H, J = 7.5, 10,2, 17.1 Hz), 5.10 d.d (1H, 2′-H, J = 0.9, 10.2 Hz), 5.25 d.d (2′-H, J = 0.9, 17.1 Hz), 6.55 d (1H, 7-H, J = 7.7 Hz), 6.82 d (1H, 6-H, J = 7.7 Hz), 6.90 s (1H, 4-H). Found, %: C 83.04; H 8.67; N 7.99. $C_{12}H_{15}N$. Calculated, %: C 83.19; H 8.73; N 8.08.

2-Ethyl-3,5-dimethyl-1*H*-indole (XX) was isolated by further elution with benzene. Yield 0.35 g (2%). The product was identified by spectral methods.

(2*S,3*R**)-1-Allyl-3,5-dimethyl-2-vinyl-2,3-dihydro-1*H*-indole (XXII).** Allyl bromide, 0.1 g, was added to a suspension of 0.139 g (0.8 mmol) of compound **XVIII** and 0.276 g of K_2CO_3 in 5 ml of methylene chloride, and the mixture was stirred, the progress of the reaction being monitored by TLC (hexane–benzene, 3:2). When initial compound **XVIII** disappeared, the mixture was diluted with 35 ml of methylene chloride and treated with 10 ml of water under stirring. The organic phase was separated and dried over K_2CO_3. The solvent was removed, and the residue was passed through a short column using benzene as eluent. Yield 0.136 g (80%), transparent liquid which turned dark on exposure to air, R_f 0.7 (C_6H_6). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 d (3H, CH_3, J = 6.7 Hz), 2.20 s (3H, CH_3), 2.95 d.q (1H, 3-H, J = 5.9, 6.7 Hz), 3.40–3.60 m (2H, CH_2), 3.80 d.d (1H, 2-H, J = 5.9, 7.5 Hz), 5.10–5.30 m and 5.75–5.90 m (6H, $CH{=}CH_2$), 6.40 d (1H, 7-H, J = 7.8 Hz), 6.79 s (1H, 4-H), 6.83 d (1H, 6-H, J = 7.8 Hz). Found, %: C 84.34; H 8.89; N 6.49. $C_{15}H_{19}N$. Calculated, %: C 84.46; H 8.98; N 6.57.

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