Reductive 1,2-Allylboration of Indoles by Triallyl- and Triprenylborane − Synthesis of 2-Allylated Indolines

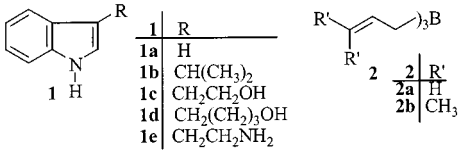
Yury N. Bubnov,*[a] Ilya V. Zhun',[a] Elena V. Klimkina,[a] Anatoly V. Ignatenko,[a] and Zoya A. Starikova[b]

Keywords: Allylboration / Reduction / Boranes / Substituted indoles / Electrocyclic reactions

Indoles undergo reductive α-allylation upon treatment with allylic boranes (triallyl- and triprenylborane) to give, after deboronation, the corresponding 2-allylated indolines in 70–85% yield. 1,2-Addition of the allylboron fragment to heterocycles occurs with full rearrangement of the allylic moiety. Reductive prenylboration of 3-substituted indoles, as well as allylboration of 3-isopropylindole, with All_3B proceed stereoselectively to produce *trans*-2,3-disubstituted indolines only, while similar reactions of triallylborane with 3-R-indoles, containing a primary group R, afford a mixture of *trans* (86–92%) and *cis* isomers (8–14%). From 1-deuterioindole and triallylborane, a mixture of *cis*- and *trans*-2-allyl-3-deuterioindole in a ratio of 1:1 was obtained. Proposed mechanism of the general reaction involves intermediate formation of 3*H*-indole tautomers followed by fast allylboration of the C=N bond. Structures of *trans*-indolines **3b** and **3c** were confirmed by X-ray analysis.

Introduction

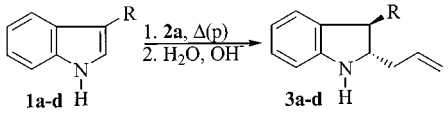
Allylic boranes readily add to the C=N bond of imines,[1−7] quinolines, phenantridine,[8] isoquinoline,[9] and 3-chloro-1-indolenines[10] to produce, after deboronation, the corresponding homoallylic amines or α-allylated dihydro heterocycles. We have recently found that pyrrole undergoes 1,2-allylboration on action of allylic triorganoboranes to form a mixture of 2-allylated *N*-boryl-3- and -4-pyrrolines.[11] Subsequent treatment of the mixture with alcohol and base affords *trans*-2,5-diallylpyrrolidine (ca. 60%) and 2-allyl-3-pyrroline (ca. 20%). Intermediate formation of 2*H*- and 3*H*-pyrrole followed by fast 1,2-allylboration of the C=N bond have been postulated as an explanation of the reductive mono- and *trans*-2,5-diallyllation of the heterocycle. Our further efforts are directed to the extension of this methodology to other aromatic heterocycles. We report herein the results concerning the reductive 1,2-allylboration of indoles **1** with triallyl- (**2a**) and triprenylborane (**2b**), and the stereochemical outcome of this useful reaction.



[a] N. D. Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences,
117913, 47 Leninsky prosp., Moscow, Russia
Fax: (internat.) + 7-095/135-5328
E-mail: bor@cacr.ioc.ac.ru
[b] A. N. Nesmeyanov Institute of Ograno-Element Compounds of Russian Academy of Sciences,
28 Vavilova st., 117813 Moscow, Russia

Results and Discussion

The reaction of indole (**1a**) with borane **2a** (1:1) gave 2-allylindoline (**3a)** (Scheme 1; Table 1, Entry 1).



Scheme 1. Reductive allylboration of indoles **1a−d**

Table 1. Synthesis of 2-allylated indolines **3a−e** and **4a**,**b**

Entry	Starting indole	Borane	1/2	*T* [°C] (*t* [h])	Product	Yield [%]	*trans*/*cis*
1	**1a**	**2a**	1:1	36 (3)[a]	**3a**	80	−
2	**1b**	**2a**	1:1	90 (2)	**3b**	58	100:0
3	**1b**	**2a**	1:1	20 (23)[b]	**3b**	68	100:0
4	**1c**	**2a**	1:3	120 (6)	**3c**	78	92:8
5	**1c**	**2a**	1:2	20 (20)[b]	**3c**	71	86:14
6	**1d**	**2a**	1:2.5	115 (2)	**3d**	84	86:14
7	**1d**	**2a**	1:2	20 (670)	**3d**	25	85:15
8	**1e**	**2a**	1:1.5	120 (5)	**3e**	64	91:9
9	**1a**	**2b**	1:1.1	120 (1.5)	**4a**	80	−
10	**1e**	**2b**	1:1.5	120 (8)	**4b**	83	100:0

[a] In Et_2O. − [b] In teflon ampoule at 7.5 kbar.

Heterocycle **3a** was transformed into benzo[*f*]pyrrolizidine by a hydroboration−oxidation−cyclization sequence.[12,13]

3-R-Indoles **1b−e** reacted with **2a** under harsher conditions than in the case of **1a**, and the stereochemistry of the 2-allyl-3-R-indolines thus obtained was found to be controlled by bulkiness of the R group (Table 1). The reactions were monitored by NMR spectroscopy and TCL.

trans-2-Allyl-3-isopropylindoline (**3b**), was obtained (58%) as the sole product from the reaction of 3-isopropyl-

  1434−193X/00/1019−3323 $ 17.50+.50/0

indole (**1b**) with triallylborane (**2a**) (1:1, 70−80 °C, 2 h), followed by deboronation, (Table 1, Entry 2). Indoline **3b** was also prepared in 68% yield by reaction of **1b** and **2a** at room temperature under high-pressure conditions (7.5 kbar, 23 h), followed by workup (Table 1, Entry 3). The structure and *trans* stereochemistry of **3b** was confirmed by X-ray analysis of its hydrobromide **3b** · HBr.

1,2-Allylboration of carbinols **1c**, and **1d**, and tryptamine (**1e**), is accompanied by boronation of OH and NH_2 groups to form the corresponding diboron compounds. Therefore, 2−3 equiv. of triallylborane (**2a**) were used per mol of **1c**−**e**. At room temperature, these reactions proceeded slowly (Table 1, Entry 7) and heating at 110−130 °C or high pressure were required.

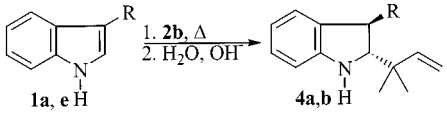
^{1}H- and ^{13}C-NMR spectra of the raw products showed the presence of two isomers in each case (Table 1, Entries 4−8). The picrate of the major isomer (*trans*-**3c**) was isolated in its pure state by recrystallization (Et_2O/MeOH) of a mixture of picrates (*trans*-**3c**/*cis*-**3c** = 92:8), and its *trans* stereochemistry was established by X-ray analysis. The crystal structure contains two crystallographically independent *trans* conformers of the cation with different orientation of CH_2CH_2OH group.

We have supposed that decreasing the reaction temperature could enhance the *trans* selectivity of the reductive 1,2-allylboration of **1c** with **2a**. For this reason, the reaction was carried out at 20 °C under high pressure (7.5 kbar, 20 h). However, the *trans*-**3c**/*cis*-**3c** ratio became 86:14 (Table 1, Entry 5). The ratio of the *trans*/*cis* isomers became 91:9 (NMR-spectroscopic data) after heating the mixture (86:14) with triallylborane (3 equiv.) at 130−140 °C for 6 h. This isomerisation seems to proceed by a deallylboration−allylboration sequence.

We failed to prepare appropriate crystals from either the picrate or hydrobromide of **3d** or **3e**. Nevertheless, ^{1}H-NMR data enabled us to assign the *trans*/*cis* ratio. Assuming that chemical shifts of 2-H and 3-H in indolines **3d** and **3e** follow the same trend as in 2,3-dimethyl-, 1,2,3-trimethyl-, and 2-methyl-3-phenylindoline,[14] as well as in **3c**, where δ(*cis*) > δ(*trans*), we concluded that the major isomers of **3d** and **3e** also have a *trans* configuration. Thus, the reductive allylboration of 3-R-indoles containing primary R groups proceeds with 86−92% *trans* stereoselectivity.

To obtain information about the mechanism of the reductive 1,2-allylboration we carried out prenylboration of indole (**1a**) and tryptamine (**1e**), as well as a reaction of triallylborane (**2a**) with 1-deuterioindole.

The reaction of **1a** with triprenylborane (**2b**) was completed in 1.5 h at 115−120 °C. 2-(1,1-Dimethylallyl)indoline (**4a**), with a terminal double bond, was obtained in 80% yield, after deboronation (Scheme 2; Table 1, Entry 9).

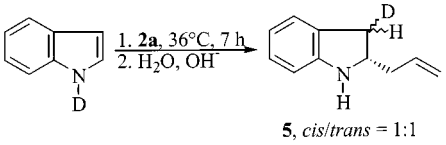


Scheme 2. Prenylboration of **1a** and tryptamine **1d**

When the same two-step process was carried out with tryptamine (**1e**) and **2b** (1:1.5, 120−130 °C, 8 h), *trans*-diamine **4b** was isolated. The absence of *cis* isomer in the crude product was shown by NMR spectroscopy. Strong NOE correlations between the 3-H proton and both CH_3 groups in the reversed prenyl function confirm the *trans* configuration of **4b**.

Formation of indolines **4a** and **4b** with a terminal double bond evidently shows that the reductive 1,2-allylboration of indoles proceeds with full rearrangement of the allylic moiety.

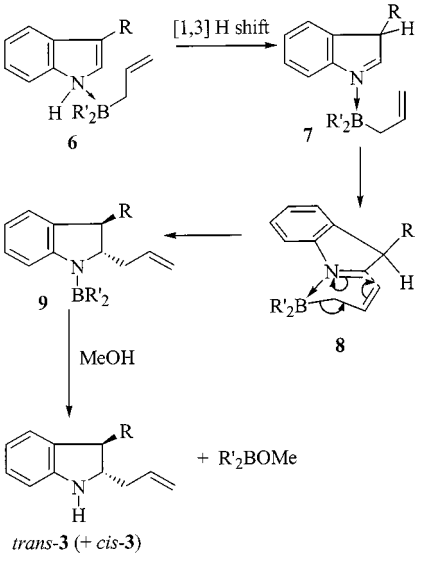
An additional important result was derived from the reaction of 1-deuterioindole and triallylborane (**2a**) (1:1, ether, 36 °C, 7 h), followed by basic hydrolysis. A 1:1 mixture of *cis*- and *trans*-2-allyl-3-deuterioindoline (**5**) was obtained in 60% yield. (Scheme 3)



5, *cis*/*trans* = 1:1

Scheme 3. Reductive α-allylation of *N*-deuterioindole with triallylborane (**2a**)

This observation shows clearly that a key stage of the reactions under consideration involves a 1,3-migration of the deuterium (or the hydrogen) atom from the nitrogen atom to C-3. The present results, as well as the previous data on the allylboration of pyrrole,[11] allow us to propose the following mechanism for the reductive 1,2-allylboration of indoles (Scheme 4).



Scheme 4. Proposed mechanism of reductive 1,2-allylboration of indoles

The N→B coordination giving adduct **6** seems to be the first step of the reaction. Then, [1,3]-sigmatropic shift of the hydrogen atom (H) from N to C-3 proceeds to generate the imine complex **7**. The C=N bond formed undergoes allylboration through a six-membered transition state **8** immediately, the allyl group being added mainly (or quantitatively) in a *trans* fashion relatively to the substituent at C-3. De-

boronation of allylated aminoborane **9** with methanol (or base) furnishes the boronate, R'_2BOMe and the α-allylated indoline *trans*-**3** (or a mixture of *cis*-**3** and *trans*-**3**).

The intermediate formation of the 3*H*-indoles has been assumed in the reactions of indoles with electrophiles.[15] Square-planar adducts Ind_2PdCl_2 with coordination of the nitrogen atom at Pd^{II} in the 3*H*-indole form have been prepared by the reaction of 2-methyl- and 2,5-dimethylindole with Na_2PdCl_4, and their structures have been characterized by X-ray analysis and spectroscopic methods.[16]

Conclusion

In conclusion, reductive 1,2-allylboration of indole and its derivatives is a general, novel reaction, leading predominantly to *trans*-2-allylated 3-R-indolines. 1,2-Addition of the allylboron fragment to indoles proceeds with full rearrangement of allylic moiety. 2-Allylated indolines thus obtained include a terminal double bond and an NH function, and may be used as starting materials for the synthesis of more complicated heterocyclic systems.

Experimental Section

General Remarks: All reactions with organoboron compounds were carried out under dry argon. − ^{1}H- and ^{13}C-NMR spectra were recorded with Bruker AC-200P and Bruker AC-300P spectrometers, chemical shifts are given relative to $SiMe_4$ (δ = 0.00). − IR spectra were taken with UR-20 spectrophotometer. − Mass spectra (MS) were taken with a Cratos MS-30 spectrometer. − Triallylborane (**2a**) was obtained from tributoxyborane and sesquiallylaluminium bromide, following a literature procedure.[17] Solvents were dried by standard procedures and distilled prior to use.

Tris(3-methylbut-2-enyl)borane (Triprenylborane, 2b): A solution of boron trifluoride−diethyl ether (20.1 g, 141 mmol) in ether (69 mL) and a solution of 1-bromo-3-methylbut-2-ene (66.4 g, 445 mmol) in ether (36 mL) were added simultaneously with stirring to magnesium turnings (12.4 g, 511 mmol) in ether (300 mL), over 2 h. The mixture was heated to reflux for 1 h. A solid precipitate (Mg and salts) was separated and extracted with hexane. The solvents were evaporated and triprenylborane (15.72 g, 51%) was obtained after two distillations, b.p. 69−70°C (1 Torr).

2-Allyl-1-diallylborylindoline (3a): A mixture of **1a** (1.9 g, 16 mmol) and **2a** (2.6 g, 20 mmol) in ether (12 mL) was heated under reflux for 3 h. Aminoborane **3a** (2.89 g, 71%) was obtained by distillation, b.p. 86−89°C (1 Torr). − n_D^{19} = 1.5512. − IR (CCl_4): ṽ = 3080, 2975, 2915, 2855, 1635, 1610, 1485, 1400, 1340, 1265, 1180, 1120, 1020, 990. − ^{1}H NMR ($CDCl_3$): δ = 1.9−2.35 (m, 6 H, $-CH_2-$ in All), 2.6−2.75 (m, 1 H, 3-H_a), 3.0−3.18 (m, 1 H, 3-H_b), 4.25−4.40 (m, 1 H, 2-H), 4.85−5.15 (m, 6 H, $=CH_2$), 5.6−5.85 (m, 1 H, 3′-H), 5.85−6.15 (m, 2 H, $B-CH_2-CH=$), 6.85−6.98 (m, 1 H in Ar), 7.0−7.25 (m, 3 H in Ar). − ^{13}C NMR ($CDCl_3$): δ = 26.8, 28.3 ($B-CH_2$), 34.1 (C-3), 40.5 (C-2′), 61.2 (C-2), 114.6, 115.1 ($B-CH_2-CH=CH_2$), 116.9 (C-5), 117.7 (C-4′), 122.8 (C-6), 125.5 (C-4), 127.0 (C-7), 133.7 (C-3a), 134.5 (C-3′), 136.3 ($B-CH_2-CH=$), 147.5 (C-7a). − ^{11}B NMR ($CDCl_3$): δ = 46.0.

General Procedure for Preparation of Allylated Indolines 3,4: Triallylborane (**2a**) or triprenylborane (**2b**) were added to the corresponding indole **1**, and the mixture was heated with stirring for 1−8 h (Table 1). Then the mixture was cooled to room temp. and worked up with 0.5−1 mL of methanol and 6 N NaOH. The organic layer was separated, and the aqueous layer extracted with ether. The combined organic layers were washed with water, and brine, and then with 1 N HCl/water solution. The acidic layer was washed with ether and treated with 6 N NaOH. The organic layer was separated, and the aqueous phase was extracted with ether. The combined organic layers were dried with K_2CO_3, the solvent was evaporated, and the residue dried in vacuo. The product thus obtained was pure by NMR, but needed to be distilled for element analysis.

2-Allylindoline (3a): 3a [2.07 g, 80%, b.p. 84−85°C (1 Torr), n_D^{19} = 1.5667] was obtained from **1a** (1.9 g, 16 mmol) and **2a** (2.6 g, 20 mmol). − MS (EI, 70 eV), *m*/*z* (%): 159 $[M]^+$ (53%), 118 $[M - C_3H_5]^+$ (100%), 117 $[M - C_3H_6]^+$ (61%), 109 $[M - C_4H_2]^+$, 91 $[C_7H_7]^+$ (60%), 65 $[C_5H_5]^+$ (26%). − IR (CCl_4): ṽ = 3495, 3400 (br.), 3080, 3060, 3035, 2980, 2935, 2905, 2850, 1640, 1610, 1485, 1465, 1450, 1400, 1370, 1315, 1245, 1150, 1010, 990, 900. − ^{1}H NMR ($CDCl_3$): δ = 2.13−2.30 (m, 2 H, $-CH_2-$ in All), 2.5−2.75 (m, 1 H, 3-H_a), 2.90−3.15 (m, 1 H, 3-H_b), 3.65−3.90 (m, 2 H, HCN, NH), 4.95−5.15 (m, 2 H, $CH_2=$), 5.6−5.85 (m, 1 H, −CH= in All), 6.40−6.70 (m, 2 H in Ar), 6.85−7.1 (m, 2H in Ar). − ^{13}C NMR ($CDCl_3$): δ = 35.3 (C-3), 40.1 (C-2′), 58.4 (HCN), 108.9 (C-5), 117.1 ($CH_2=$), 118.2 (C-6), 124.5 (C-4), 127.0 (C-7), 128.2 (C-3a), 135.0 (−CH= in All), 150.5 (C-7a). − $C_{11}H_{13}N$ (159.1): calcd. C 82.97, H 8.23, N 8.80; found C 83.00, H 8.48, N 8.70.

***trans*-2-Allyl-3-isopropylindoline (3b):** a) **3b** [0.46 g, 58%, b.p. 108−108.5°C (1 Torr), n_D^{22} = 1.5427] was synthesized from **2a** (0.76 g, 5.7 mmol) and **1b** (0.63 g, 3.9 mmol). − ^{1}H NMR ($CDCl_3$): δ = 0.95−1.15 (m, 6 H, $2CH_3$), 1.95−2.15 [m, 1 H, $CH(CH_3)_2$], 2.25−2.4 (m, 2 H, CH_2 in All), 2.9−3.05 (m, H, 3-H), 3.6−3.8 (m, 1 H, 2-H), 3.95 (br. s, NH), 5.1−5.3 (m, 2 H, $=CH_2$), 5.8−6.1 (m, H, =CH-), 6.7 (d, 1 H in Ar), 6.8 (t, 1 H in Ar), 7.1−7.3 (m, 2 H in Ar). − ^{13}C NMR ($CDCl_3$): δ = 18.9 (CH_3), 19.5 (CH_3), 32.0 [$CH(CH_3)_2$], 41.8 (C-3), 54.0 (CH_2), 59.7 (C-2), 108.9 (CH in Ar), 117.5 (=CH−), 117.7 (CH in Ar), 125.1 (CH in Ar), 127.4 (CH in Ar), 130.1 (C_{quat}), 134.9 ($=CH_2$), 150.3 ($C_{quat}-N$). − $C_{14}H_{19}N$ (201.3): calcd. C 83.53, H 9.51, N 6.96; found C 83.53, H 9.57, N 6.98. − b) A mixture of **1b** (0.42 g, 2.6 mmol) and **2a** (0.54 g, 4.0 mmol) was kept at room temp. and 7.5 kbar in a 2-mL Teflon ampoule during 23 h. The mixture was then treated in the usual way, and 0.36 g (68%) of *trans*-**3b** was obtained.

***trans*-2-Allyl-3-isopropylindolinium Bromide (3b·HBr):** This compound was synthesized from **3b** (0.54 g, 2.7 mmol) and 1 N solution of HBr (3 mL, 3 mmol) in ether (10 mL). After decantation and recrystallisation, monocrystals of **3b·HBr** [m.p. 106−108°C (from ether/methanol)] were obtained.

2-Allyl-3-(2-hydroxyethyl)indoline (3c): a) **3c** [2.87 g, 78%, b.p. 131−134°C (0.5 Torr), n_D^{20} = 1.5725] was obtained from **1c** (2.90 g, 18.0 mmol) and **2a** (7.82 g, 58.4 mmol). − IR (KBr): ṽ = 3350 (OH, NH), 2937 (CH_2), 1640, 1610, 1480, 1469, 1435, 1400, 1325, 1255, 1059, 1026, 1000, 924 ($CH=CH_2$), 758. − ^{1}H NMR ($CDCl_3$): δ = 1.85−2.0 (m, 2 H, CH_2), 2.2−2.35 (m, 2 H, CH_2OH), 3.0 (br. s, OH), 3.1−3.2 (m, H, 3-H in *trans* isomer), 3.3−3.4 (m, 3-H in *cis* isomer), 3.55−3.7 (m, 3 H, 2-H in *trans* isomer and CH_2 in All), 3.8−3.9(m, 1 H, 2-H in *cis* isomer), 4.0 (br. s, NH), 5.1−5.2 (m, 2 H, $=CH_2$), 5.75−5.9 (m, H, =CH−), 6.65 (d, 1 H in Ar), 6.75 (t, 1 H in Ar), 7.0−7.15 (m, 2 H in Ar). − ^{13}C NMR ($CDCl_3$): main set of signals (*trans* isomer): δ = 37.4 (CH_2), 40.3 (CH_2), 44.4 (C-3), 60.0 (CH_2OH), 63.6(C-2), 109.7 (CH in Ar), 117.8 (=CH−),

118.8 (CH in Ar), 124.5 (CH in Ar), 127.6 (CH in Ar), 131.3 (C_{quat}), 134.8 (=CH_2), 149.5 (C_{quat}−N); minor (*cis*) isomer signals set: δ = 30.8 (CH_2), 34.3 (CH_2), 41.1 (C-3), 60.1 (CH_2OH), 62.0(C-2), 110.0 (CH in Ar), 117.7 (=CH−), 119.0 (CH in Ar), 124.4 (CH in Ar), 127.5 (CH in Ar), 132.2 (C_{quat}), 135.6 (=CH_2), 149.9 (C_{quat}−N). The ratio of *trans*-**3c**/*cis*-**3c** isomers was 92:8. − $C_{13}H_{19}NO$ (205.3): calcd. C 76.81, H 8.43, N 6.89; found C 76.90, H 8.48, N 6.91. − b) A mixture of **1c** (0.33 g, 2.0 mmol) and **2a** (0.84 g, 6.3 mmol) was stirred at 50°C for 15 min (until the propene elimination was complete). The mixture was placed into a 2-mL Teflon ampoule and kept at room temp. at 7.5 kbar during 20 h. After workup, **3c** was obtained (0.30 g, 71%). The ratio of *trans*-**3c**/*cis*-**3c** isomers was 86.5:13.5.

***cis*−*trans* Isomerisation of 2-Allyl-3-(2-hydroxyethyl)indoline (3c):** A mixture of 0.30 g (1.5 mmol) of **3c** obtained under high-pressure conditions (content of *cis* isomer 14%, see above) and **2a** (0.60 g, 4.5 mmol) was heated for 6 h at 120−140°C. Compound **3c** was recovered after workup. The ratio of *trans*-**3c**/*cis*-**3c** isomers was 91.5:8.5.

2-Allyl-3-(2-hydroxyethyl)indolinium Picrate (3c·Pic): Compound **3c** (0.20 g, 1.0 mmol) and picric acid (0.22 g, 1.0 mmol) were heated under reflux in methanol for 30 min. After evaporation of the solvent and recrystallisation, monocrystals of **3c·Pic** were obtained (m.p. 110−111.5°C).

2-Allyl-3-(4-hydroxybutyl)indoline (3d): a) **3d** [4.85 g, 84%, b.p. 180°C (0.5 Torr), n_D^{20} = 1.5610] was synthesized from **1d** (4.70 g, 24.8 mmol) and **2a** (9.24 g, 51.7 mmol). − IR (KBr): ν̃ = 3360 (OH, NH), 2939 (CH_2), 2863 (CH_2), 1640, 1610, 1480, 1469, 1440, 1405, 1330, 1255, 1060, 1026, 1000, 924 (CH=CH_2), 755. − ^{1}H NMR ($CDCl_3$): δ = 1.45−1.65 (m, 6 H, 3CH_2), 2.2−2.35 (m, 2 H, CH_2OH), 2.95 (q, H, 3-H in *trans* isomer), 3.20 (q, H, 3-H in *cis* isomer), 3.55 (m, H, 2-H in *trans* isomer), 3.60 (t, 2 H, CH_2 in All), 3.8 (m, H, 2-H in *cis* isomer), 3.9−4.0 (br. s, NH), 5.1−5.3 (m, 2 H, =CH_2), 5.75−5.90 (m, H, =CH−), 6.61 (d, 1 H in Ar), 6.7 (t, 1 H in Ar), 7.0−7.1 (m, 2 H in Ar). − ^{13}C NMR ($CDCl_3$): main set of signals (*trans* isomer): δ = 23.0 (CH_2), 32.7 (CH_2), 34.4 (CH_2), 40.7 (CH_2), 47.4 (C-3), 62.3(*C*H_2OH), 63.4(C-2), 109.2 (CH in Ar), 117.5 (=CH−), 118.2 (CH in Ar), 124.3 (CH in Ar), 127.4 (CH in Ar), 132.0 (C_{quat}), 135.0 (=CH_2), 149.7 (C_{quat}−N); minor (*cis*) isomer signals set: δ = 23.8 (CH_2), 27.4 (CH_2), 34.0 (CH_2), 44.2 (C-3), 61.7(C-2), 109.6 (CH in Ar), 118.5 (CH in Ar), 124.1 (CH in Ar), 132.6 (C_{quat}), 135.6 (=CH_2), 149.9 (C_{quat}−N). The ratio of *trans*-**3d**/*cis*-**3d** isomers was 86:14. − $C_{15}H_{23}NO$ (233.4): calcd. C 77.88, H 9.15, N 6.05, found C 77.82, H 9.37, N 5.98. − b) **1d** (3.8 g, 20 mmol) and **2a** (5.6 g, 41 mmol) were mixed together, and stirred at 50°C for 30 min (until the propene elimination was complete). The mixture was kept at room temp. for 28 d (672 h). The mixture was then worked up in the usual way. Compound **3d** (1.14 g, 25%) was obtained by distillation, b.p. 174−177 °C (0.5 Torr). The ratio of *trans*-**3d**/*cis*-**3d** isomers was 85:15.

2-Allyl-3-(2-aminoethyl)indoline (3e): 3e [2.45 g, 64%, b.p. 134−136°C (0.5 Torr), n_D^{20} = 1.5782] was obtained from **2a** (3.81 g, 28.4 mmol) and **1e** (3.00 g, 18.7 mmol). − IR (KBr): ν̃ = 3380 (NH), 3260 (NH_2), 2925 (CH_2), 2857 (CH_2), 1640, 1610, 1480, 1469, 1435, 1400, 1325, 1255, 1026, 1000, 924 (CH=CH_2), 755. − ^{1}H NMR ($CDCl_3$): δ = 1.8 (m, 2 H, CH_2), 2.3 (m, 2 H, C$H_2$$NH_2$), 2.85 (t, CH_2 in All), 3.05 (m, H, 3-H in *trans* isomer), 3.2 (m, H, 3-H in *cis* isomer), 3.55 (m, H, 2-H in *trans* isomer), 3.8 (m, H, 2-H in *cis* isomer), 5.1 (t, 2 H, =CH_2), 5.85 (m, H, =CH−), 6.55 (d, 1H in Ar), 6.7 (t, 1H in Ar), 7.05 (m, 2H in Ar). − ^{13}C NMR ($CDCl_3$): main set of signals (*trans* isomer): δ = 38.6 (CH_2), 39.5 (CH_2), 40.5 (CH_2), 44.9 (C-3), 63.6(C-2), 108.9 (CH in Ar), 117.4 (=CH−), 118.0 (CH in Ar), 124.1 (CH in Ar), 127.3 (CH in Ar), 131.5 (C_{quat}), 134.8 (=CH_2), 149.7 (C_{quat}−N); minor (*cis*) isomer signals set: δ = 31.7 (CH_2), 34.1 (CH_2), 40.2 (CH_2), 41.7 (C-3), 61.7 (C-2), 109.2 (CH in Ar), 118.2 (=CH−), 124.0 (CH in Ar), 127.2 (CH in Ar), 132.1 (C_{quat}), 135.4 (=CH_2), 149.9 (C_{quat}−N). The ratio of *trans*-**3e**/*cis*-**3e** isomers was 91:9. − $C_{13}H_{20}N_2$ (204.3): calcd. C 77.18, H 8.97, N 13.85; found C 76.88, H 9.02, N 13.90.

2-(1,1-Dimethylprop-2-enyl)indoline (4a): 4a [2.17 g, 82%, b.p. 81−83°C (0.5 Torr), n_D^{20} = 1.5545] was synthesized from **1a** (1.66 g, 14.0 mmol) and **2a** (3.50 g, 15.6 mmol). − IR (KBr): ν̃ = 3375 (NH), 2983 (CH_2), 2870 (CH_2), 1638, 1609, 1490, 1469, 1415, 1405, 1380, 1363, 1320, 1255, 1065, 1025, 1010, 920 (CH=CH_2), 753, 590, 425. − ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 6 H, 2 CH_3), 2.9−3.1 (m, 2 H, 3-H), 3.85 (t, 1 H, 2-H), 3.95 (br. s, 1 H, NH), 5.2 (dd, 2 H, =CH_2), 6.0 (dd, 1 H, =CH− in *i*Pren), 6.65−6.8 (m, 2 H in Ar), 7.1−7.2 (m, 2 H in Ar). − ^{13}C NMR ($CDCl_3$): δ = 21.8 (CH_3), 24.1 (CH_3), 31.3 (C-3), 40.1 (C_{quat}), 67.7 (C-2), 108.4, 112.4 (CH in Ar), 117.9 (=CH− in *i*Pren), 124.4, 127.1 (CH in Ar), 128.7 (C-3a), 145.5 (=CH_2), 151.2 (C-7a). − $C_{15}H_{17}N$ (211.3): calcd. C 83.37, H 9.15, N 7.48; found C 83.29, H 9.16, N, 7.61.

***trans*-3-(2-Aminoethyl)-2-(1,1-dimethylprop-2-enyl)indoline (4b): 4b** [1.80 g, 83%, b.p. 123−127°C (0.5 Torr), n_D^{20} = 1.5679] was obtained from **1e** (1.50 g, 9.4 mmol) and **2a** (2.99 g, 13.8 mmol). − IR (KBr): ν̃ = 3370 (NH), 3280 (NH_2), 3080, 3055, 3033, 2984 (CH_2), 2963 (CH_3), 2878 (CH_2), 1637, 1609, 1490, 1469, 1418, 1382, 1365, 1325, 1260, 1060, 1025, 1013, 920 (CH=CH_2), 752, 742, 690. − ^{1}H NMR ($CDCl_3$): δ = 0.9 (s, 3 H, CH_3), 1.0 (s, 3 H, CH_3), 1.3 (br. s, NH_2), 1.75 (q, 2 H, CH_2), 2.75−2.85 (m, 2 H, C$H_2$$NH_2$), 3.1−3.2 (m, 1 H, 3-H), 3.25 (d, 1 H, 2-H), 4.0 (br. s, 1 H, NH), 5.0−5.1 (m, 2 H, =CH_2), 5.7−5.85 (q, H, =CH− in *i*Pren), 6.5 (d, 1 H in Ar), 6.65 (t, 1 H in Ar), 7.0 (m, 2 H in Ar). − ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 22.5 (CH_3), 39.3 (CH_2NH_2), 41.0 (C-3), 41.1 (CH_2), 41.7 (C_{quat}), 71.2 (C-2), 107.6, 112.7 (CH in Ar), 117.4 (=CH− in *i*Pren), 123.9, 127.3 (CH in Ar), 131.9 (C-3a), 145.2 (=CH_2), 150.5 (C-7a). − $C_{15}H_{25}N_2$ (233.4): calcd. C 78.21, H 9.63, N 12.16; found C 78.45, H 9.62, N 12.09.

1-Deuterioindole: Indole (0.50 g, 4.3 mmol) was dissolved in MeOD (1.00 mL, 24.6 mmol) and the mixture was stirred at room temp. for 1 h. The alcohol was removed under vacuum, and the residue was dissolved in another 1 mL MeOD. After 1 h at room temp., the alcohol was evaporated and 1-deuterioindole (0.5 g, 89% purity) was obtained. − ^{1}H NMR ($CDCl_3$): δ = 6.3 (1 H, d), 7.0−7.2 (3 H, m), 7.4 (1 H, d), 7.7 (1 H, d), 8.1 (NH in indole, br. s, *I* = 0.11).

2-Allyl-3-deuterioindolines (5a and 5b): A mixture of **2a** (0.67 g, 5.0 mmol) and deuterioindole (0.50 g, 4.2 mmol) in ether (6 mL) was heated under reflux for 7 h. Then, MeOH (0.6 mL) and 5 N NaOH (2 mL) were added. The amines were extracted with ether and dried with K_2CO_3. Indole was removed by chromatography on SiO_2 with ether as eluent. A mixture of *trans*- (**5a**) and *cis*-2-allyl-3-deuterioindoline (**5b**) [0.41 g, 60%, b.p. 85−87°C (1 Torr)] was obtained by distillation. − ^{1}H NMR ($CDCl_3$): δ = 2.1−2.4 (m, 2 H, CH_2 in All), 2.5−2.65 (m, 0.5 H, 3-H in *trans* or *cis* isomer), 2.9−3.05 (m, 0.5 H, 3-H in *trans* or *cis* isomer), 3.6−3.90 (m, 2 H, HCN, NH), 4.9−5.2 (m, 2 H, CH_2=), 5.6−5.85 (m, 1 H, −CH= in All), 6.45−6.80 (m, 2 H in Ar), 6.95−7.15 (m, 2 H in Ar). − ^{2}H NMR ($CDCl_3$): δ = 2.92 (s, 0.5 D, D-3 in *trans* or *cis* isomer), 3.32 (s, 0.5 D, D-3 in *trans* or *cis* isomer). − ^{13}C NMR ($CDCl_3$): δ = 34.6, 35.0, 35.3 (C-3, J_{C-D} = 32 Hz), 40.6 (C-2′), 58.3 (HCN), 109.1

(C-5), 117.2 (CH_2=), 118.4 (C-6), 124.6 (C-4), 127.1 (C-7), 128.3 (C-3a), 134.9 (−CH= in All), 150.4 (C-7a). The ratio of **5a/5b** was 1:1.

X-ray Crystallographic Study: Both structures of **3b·HBr** and **3c·Pic** were solved by direct methods and refined by full-matrix least-squares technique in anisotropic approximation. All H atoms (except hydrogen atoms in the NH_2^+ group in **3b·HBr** which were refined in isotropic approximation) were placed in the geometrically calculated positions and included in the refinement using the rigid-model approximation with the $U_{iso}(H)=1.3\cdot U_{eq}(C)$ for the methylene and $U_{iso}(H)= 1.5\cdot U_{eq}(C)$ for methyl groups, where $U_{eq}(C)$ is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding H atom. The oxygen atoms in the disordered NO_2 groups in **3c·Pic** were refined with the site occupancy factors equal to 0.6 and 0.4. All calculations were carried out wit an IBM PC with the help of SHELXTL PLUS 5 program package.[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136225 for **3b·HBr** and CCDC-136226 for **3c·Pic**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was partly supported by the Russian Foundation for Basic Research (grant 99-03-33125a), the Council of Grants and Support of Leading Scientific Schools of the President of the Russian Federation (grant No. 96-15-97289), and Ministry of Science and Technology of Russian Federation (grant 04.02.09.01).

[1] A. Meller, G. Gerger, *Monatsh. Chem.* **1974**, *105*, 684−688.
[2] R. W. Hoffmann, G. Eichler, A. Endesfelder, *Liebigs Ann. Chem.* **1983**, 2000−2007.
[3] [3a] Y. Yamamoto, S. Nishii, K. Maruyama, T. Kamatsu, W. Ito, *J. Am. Chem. Soc.* **1986**, *108*, 7778−7786 − [3b] Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207−2293.
[4] Yu. N. Bubnov, V. C. Bogdanov, B. M. Mikhailov, *Zh. Obshch. Khim.* **1968**, *38*, 260−267 [*Chem. Abstr.*, **1968**, *69*, 52200j].
[5] [5a] Yu. N. Bubnov, V. I. Zheludeva, T. Yu. Rudashevskaya, T. S. Kuznetsova, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1179−1182 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, *38*, 1073−1075 (Engl. Transl.)] − [5b] L. I. Lavrinovich, A. V. Ignatenko, Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.* **1992**, 2597−2604 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.* **1992**, *41*, 2051−2057 (Engl. Transl.)] − [5c] M. E. Gurskii, S. B. Golovin, A. V. Ignatenko, Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.* **1992**, 2198−2199 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.* **1992**, *41*, 1724 (Engl. Transl.)] − [5d] M. E. Gurskii, T. V. Potapova, Yu. N. Bubnov, *Izv. Acad. Nauk, Ser. Khim.* **1998**, 1450−1452 [*Russ. Chem. Bull.* **1998**, *47*, 1410−1412 (Engl. Transl.)].
[6] [6a] Sh. Itsuno, K. Watanabe, K. Ito, A. A. El-Shehaway, A. Sharhan, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 109−110 − [6b] A. A. El-Shehway, M. Y. Abdelaal, K. Watanabe, K. Ito, Sh. Itsuno, *Tetrahedron: Asymmetry* **1997**, *8*, 1731−1734.
[7] [7a] Yu. N. Bubnov, *Pure Appl. Chem.* **1994**, *66*, 235−244 − [7b] Yu. N. Bubnov, in: *Current Topics in the Chemistry of Boron* (Ed.: G. Y. Kabalka), Royal Society of Chemistry, Thomas Graham House, Cambridge, **1994**, p. 44−55 − [7c] Yu. N. Bubnov, *Izv. Acad. Nauk, Ser. Khim.* **1995**, 1203−1216 [*Russ. Chem. Bull.* **1995**, *44*, 1156−1170 (Engl. Transl.)].
[8] Yu. N. Bubnov, S. V. Evchenko, A. V. Ignatenko, *Izv. Acad. Nauk, Ser. Khim.* **1992**, 2815−2816 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.* **1992**, *41*, 2239−2240 (Engl. Transl.)].
[9] Yu. N. Bubnov, S. V. Evchenko, A. V. Ignatenko, *Izv. Acad. Nauk, Ser. Khim.* **1993**, 1325−1326 [*Russ. Chem. Bull.* **1993**, *42*, 1268−1269 (Engl. Transl.)].
[10] [10a] K. M. Depew, S. J. Danishefsky, N. Rosen, L. Sepp-Lorenzino, *J. Am. Chem. Soc*. **1996**, *118*, 12463−12464 − [10b] J. M. Shkeryantz, J. C. G. Woo, S. J. Danishefsky, *J. Am. Chem. Soc*. **1995**, *117*, 7025−7026.
[11] Yu. N. Bubnov, E. V. Klimkina, L. I. Lavrinovich, A. Yu. Zykov, A. V. Ignatenko, *Izv. Acad. Nauk, Ser. Khim.* **1999**, 1718−1728 [*Russ. Chem. Bull.* **1999**, *48*, 1696−1706 (Engl. Transl.)]. And references cited therein.
[12] Yu. N. Bubnov, M. E. Gurskii, T. V. Potapova, *Izv. Acad. Nauk, Ser. Khim.* **1996**, 2807−2808 [*Russ. Chem. Bull.* **1996**, *45*, 2665−2667 (Engl. Transl.)].
[13] Yu. N. Bubnov, in: *Advances in Boron Chemistry* (Ed. W. Siebert), The Royal Society of Chemistry, Thomas Graham House, Cambridge, **1997**, p. 123−138.
[14] [14a] C. C. Mclomas, E. J. Gilbert, D. L. Van Vranken, *J. Org. Chem.* **1997**, *62*, 8600−8603 − [14b] M. Riviere, N. Paillous, A. Lattes, *Bull. Soc. Chim. Fr.* **1974**, 1911−1916 − [14c] F. A. L. Anet, J. M. Muchowski, *Chem. Ind. (London)* **1963**, 81−82.
[15] *Indoles, Parts 1, 2, 3* (Ed.: W. J. Houlihan), John Wiley and Sons, New York, **1972**, **1979**.
[16] O. Yamauchi, M. Takani, K. Toyoda, H. Masuda, *Inorg. Chem.* **1990**, *29*, 1856−1860.
[17] L. I. Zakharkin, V. I. Stanko, *Izv. AN SSSR, OHN* **1960**, 1896−1898 [*Chem. Abstr.* **1961**, *55*, 15337d].
[18] G.M. Sheldrick, *SHELXTL Ver.5.0.*, Software Reference Manual, Siemens Industrial Automation, Inc., Madison, **1994**.

Received December 14, 1999
[O99673]