Reductive *trans*-1,3-dialkylation of isoquinoline on treatment with RLi and triallylborane*

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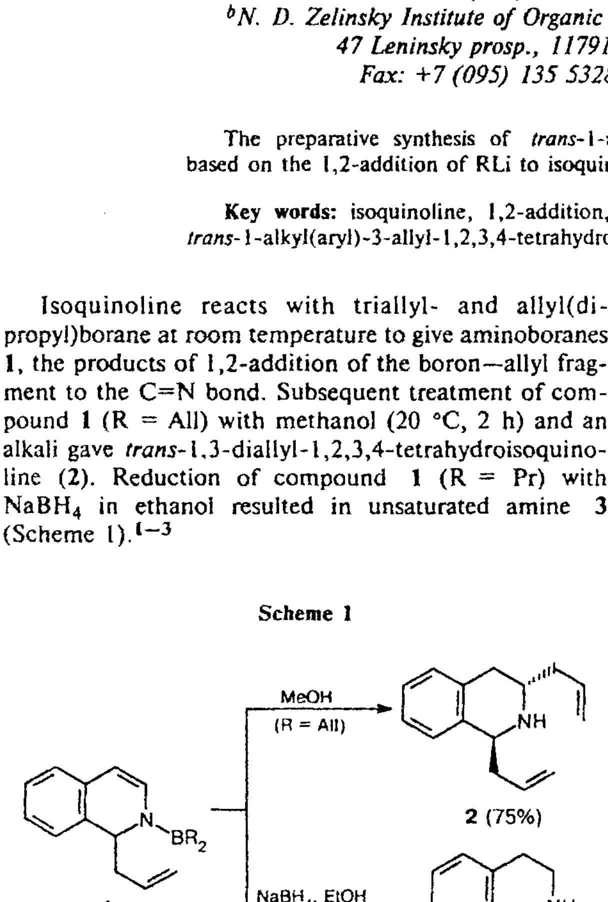
The preparative synthesis of *trans*-1-alkyl(aryl)-3-allyl-1,2,3,4-tetrahydroisoquinolines based on the 1,2-addition of RLi to isoquinoline and *trans*-allylboration is described.

Key words: isoquinoline, 1,2-addition, alkyl(aryl)lithium; allylboration, triallylborane; *trans*-1-alkyl(aryl)-3-allyl-1,2,3,4-tetrahydroisoquinolines, stereochemistry.

Isoquinoline reacts with triallyl- and allyl(dipropyl)borane at room temperature to give aminoboranes **1**, the products of 1,2-addition of the boron—allyl fragment to the C=N bond. Subsequent treatment of compound **1** (R = All) with methanol (20 °C, 2 h) and an alkali gave *trans*-1,3-diallyl-1,2,3,4-tetrahydroisoquinoline (**2**). Reduction of compound **1** (R = Pr) with $NaBH_4$ in ethanol resulted in unsaturated amine **3** (Scheme 1).[1-3]

Scheme 1



1

2 (75%)

3 (84%)

It has been shown recently that successive treatment of pyridine with alkyl- or phenyllithium, triallylborane, and an alcohol gives *trans*-2-allyl-6-alkyl(phenyl)-1,2,3,6-tetrahydropyridines.[4,5] The latter are transformed almost quantitatively into the corresponding *cis*-isomers on heating (160—195 °C) with triallylborane.[5,6]

In a continuation of studies in this field, we developed a preparative method for the synthesis of *trans*-1-alkyl(aryl)-3-allyl-1,2,3,4-tetrahydroisoquinolines (**4a—c**) based on a combination of 1,2-addition of RLi to isoquinoline and *trans*-allylboration (Scheme 2).

According to GLC analyses and NMR spectroscopy data, the yields of amines **4** exceed 90% (see below), with the preparative yields ranging from 55 to 70%.

The transformation of isoquinoline into amines **4** is a multistage process, which involves a series of successive reactions as shown in Scheme 2.

Probably, the *N*-lithium derivative **5**, which results from the addition of RLi to isoquinoline,[7,8] forms the corresponding ate-complex **6** with triallylborane. The protolytic cleavage of the B—N bond in this complex involves an allyl-type rearrangement and results in an imine complex of triallylborane **7**. The C=N bond in the latter undergoes instant allylboration through the six-centered intermediate **8**. The addition of the allyl fragment occurs stereoselectively, namely at the *trans*-position relative to the R group. Deboration of the resulting aminoborane **9** with an excess of methanol and an alkali gives the target amine **4**, in which the substituents are *trans* relative to the heterocycle.

It was found that the series of reactions leading to amines **4** (see Scheme 2) is accompanied by a side process, namely, the formation of the corresponding 1-R-isoquinolines (5—6% according to GLC analyses). The latter result from the aromatization (disproportionation or oxidation) of *N*-lithium adducts **5**. Thus, the raw product of the reaction with MeLi contains amine **4a** (95%) along with 1-methylisoquinoline (5%), while amine **4b** obtained from Bu^nLi contains 6% of 1-butylisoquinoline.

Because hydrochlorides **4a** · HCl and **4b** · HCl are virtually insoluble in water, separation of the admixture

* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1206—1209, June, 1998.

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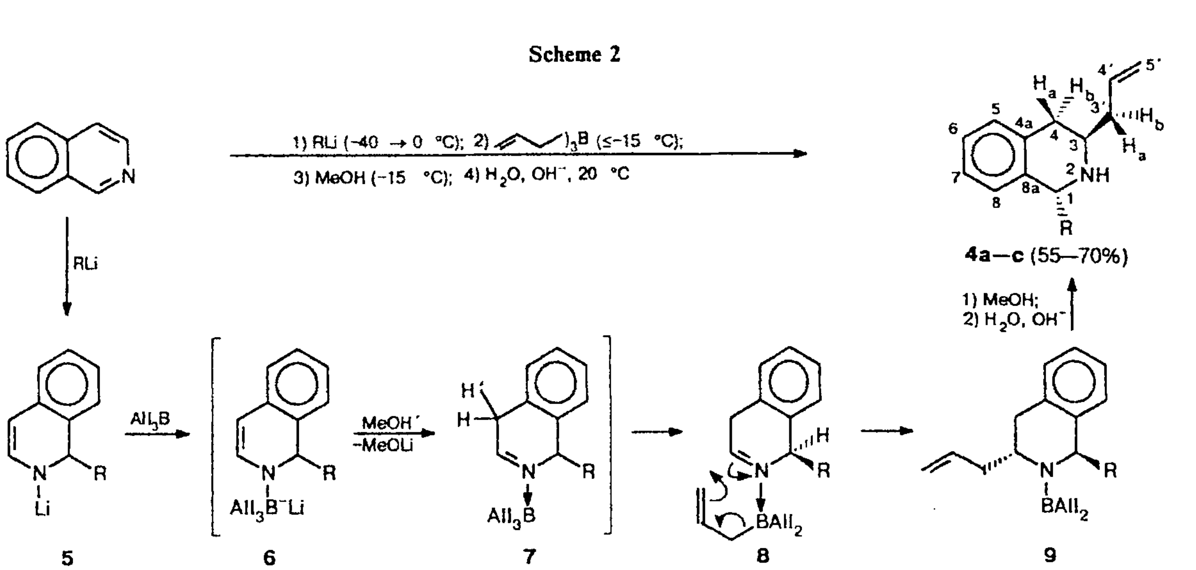
Scheme 2

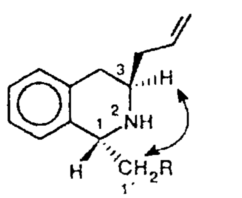


R = Me (**a**), Bu^n (**b**), Ph (**c**)

of the corresponding 1-R-isoquinolines and isolation of amines **4a** and **4b** do not present serious problems. For example, work-up of a mixture of compound **4a** and 1-methylisoquinoline with 2 *N* HCl produces a precipitate of solid **4a** · HCl, whereas isoquinolinium hydrochloride is transferred to the aqueous phase. Free amine **4a** is obtained by treatment of recrystallized salt **4a** · HCl with boiling 20% NaOH followed by extraction with pentane. Amine **4b** was isolated in a similar way (60%).

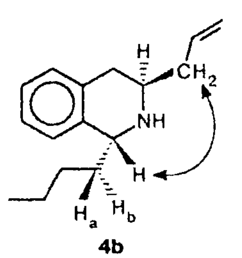
The structure of compounds **4a—c** was confirmed by elemental analyses and by physicochemical methods (^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry). The signals in the NMR spectra were assigned on the basis of ^{1}H—^{1}H COSY-45 spectra.

The *trans*-configuration of amines **2** and **4a—c** was determined by two-dimensional phase-sensitive 2D NOESY spectroscopy.

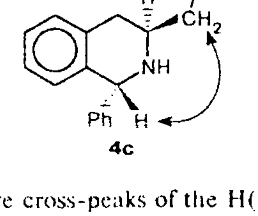


2, 4a

R = H (**4a**), CH=CH$_2$ (**2**)



4b



4c

The positive cross-peaks of the H(3) proton with the Me group (**4a**), H(3) with C(1')H$_2$ of the allyl group (**2**), and H(1) with CH$_2$ of the allyl group (**4b** and **4c**) indicate unambiguously the *trans*-arrangement of the substituents in molecules **2** and **4a—c**.

The stereoselective method for the synthesis of the hitherto unknown *trans*-1-R-3-allyl-1,2,3,4-tetrahydroisoquinolines **4** described in this paper opens up wide prospects in the isoquinoline chemistry. The presence of an NH$_2$ group, a double bond, and a benzene ring in amines **4** will provide the possibility of performing various subsequent functionalizations of these compounds, *e.g.*, they can be used as the starting compounds for the synthesis of tricyclic systems with a ring junction N atom by closing a five-membered cycle (as it was done in the case of other α-allylated heterocyclic systems[9,10]). Moreover, it can be assumed that *trans*- and/or *cis*-1,3-disubstituted tetrahydroisoquinolines are produced by some plant and animal organisms and can be found in natural objects.

Experimental

All operations with organoboron compounds were carried out in a dry argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer in CDCl$_3$. ^{1}H—^{1}H COSY and 2D NOESY spectra were recorded on a Bruker AMX-400 instrument using SiMe$_4$ as the internal standard. IR spectra were obtained on a UR-20 spectrophotometer. Mass spectra (EI, 70 eV) were recorded on a Varian-MAT spectrometer. GLC analyses were carried out on a Khrom-5 instrument with an OV-1 column (1 m), Chromaton as the stationary phase, and helium as the carrier gas.

***trans*-3-Allyl-1-methyl-1,2,3,4-tetrahydroisoquinoline (4a).** A 2.03 *N* solution of methyllithium (15 mL, 30.45 mmol) in ether was placed in a three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an inlet for argon. Anhydrous THF (16 mL) and a solution of isoquinoline (3.93 g, 30.5 mmol) in anhydrous THF (16 mL) were successively added with cooling (0 °C). The reaction mixture was stirred for 1 h at 20 °C, triallylborane (4.08 g, 30.5 mmol) was added at −15 °C, and the solution was gradually (in 1 h) heated to 10 °C. After that, anhydrous MeOH (5 mL, 124 mmol) and then 20% NaOH (13 mL) were cautiously added at −15 °C. The organic layer was separated, and the aqueous layer was extracted with ether (3×10 mL). The low-boiling compounds were distilled off; the residue contained 95% of compound **4a** and 5% of 1-methylisoquinoline (according to GLC data). Ether (20 mL) and 5 *N* HCl (4.7 mL) were added to the above mixture. The remaining salt, which was insoluble in water and in ether, was filtered off and recrystallized from an ethyl acetate—Pr^{i}OH mixture to give 4.93 g (73%) of hydrochloride **4a** · HCl, m.p. 209—210 °C. The resulting salt was treated with boiling 20% NaOH solution until it was completely dehydrochlorinated. The aqueous layer was extracted with pentane, and the extract was dried with K_2CO_3. The solvents were concentrated *in vacuo*. Distillation of the residue gave amine **4a**, b.p. 102 °C (1 Torr), n_D^{19} 1.5419. Found (%): C, 83.44; H, 9.21; N, 7.32. $C_{13}H_{17}N$. Calculated (%): C, 83.37; H, 9.15; N, 7.48. IR (pure compound), ν/cm^{-1}: 3300 (br), 3080, 3020, 2970, 2920, 2830, 1640, 1490, 1445, 1370, 1330, 1200, 1200, 1140, 1040, 1000, 920, 830, 760, 735, 675, 630, 600, 535, 450. ^{1}H NMR (400 MHz), δ: 1.38 (d, 3 H, CH_3, J = 6.9 Hz); 1.91 (br.s, 1 H, NH); 2.22 (m, 2 H, H(3′)); 2.45 (dd, 1 H, H_a(4), ^2J = 16.2 Hz, ^3J = 9.9 Hz); 2.72 (dd, 1 H, H_b(4), ^2J = 16.2 Hz, ^3J = 4 Hz); 3.15 (m, 1 H, H(3)); 4.15 (q, 1 H, H(1), ^3J = 6.9 Hz); 5.09 (m, 1 H, H_a(5′)); 5.13 (m, 1 H, H_b(5′)); 5.81 (m, 1 H, H(4′)); 7.02 (m, 2 H, Ph); 7.08 (m, 2 H, Ph). ^{13}C NMR, δ: 23.60 (CH_3); 35.04 (C(4)); 40.23 (C(3′)); 46.07 (C(3)); 50.15 (C(1)); 116.93 (C(5′)); 125.20, 125.45, 126.18 (C(5), C(6), C(7)); 128.65 (C(8)); 133.71 (C(4a)); 134.84 (C(4′)); 139.64 (C(8a)). MS, *m/z*: 187 [M]$^+$, 146 [M−C_3H_5]$^+$.

***trans*-3-Allyl-1-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (4a · HCl).** M.p. 209—210 °C (from an ethyl acetate—Pr^{i}OH mixture). IR (pellets with KBr), ν/cm^{-1}: 3420 (br), 2940, 2710, 2500, 1590, 1500, 1450, 1395, 1360, 1090, 1040, 1000, 935, 790, 740, 455, 405. ^{1}H NMR (200 MHz), δ: 1.80 (d, 3 H, CH_3); 2.45—2.8 (m, 1 H, H_a(3′)); 2.9—3.3 (m, 3 H, H(4), H_b(3′)); 3.5—3.8 (m, 1 H, H(3)); 4.6—4.9 (m, 1 H, H(1)); 5.1—5.5 (m, 2 H, H(5′)); 5.7—6.1 (m, 1 H, H(4′)); 7.0—7.4 (m, 4 H, Ph); 9.95 (br.s, 2 H, NH_2^+). ^{13}C NMR, δ: 20.57 (CH_3); 30.60 (C(4)); 35.98 (C(3′)); 48.61 (C(3)); 49.98 (C(1)); 119.54 (C(5′)); 126.08, 126.86, 127.50 (C(5), C(6), C(7)); 128.95 (C(8)); 130.20 (C(4a)); 131.59 (C(4′)); 133.09 (C(8a)).

***trans*-3-Allyl-1-butyl-1,2,3,4-tetrahydroisoquinoline (4b).** Isoquinoline (6.6 g, 51.2 mmol) was added at −40 °C to a mixture of a 1.28 *N* solution of *n*-butyllithium (40 mL, 51.2 mmol) in hexane and anhydrous ether (20 mL). The mixture was stirred for 0.5 h at −30 °C, and triallylborane (6.86 g, 51.2 mmol) was then added. The solution temperature was brought to 5 °C in 1.5 h, the solution was cooled to −30 °C, and anhydrous MeOH (8.3 mL, 204.8 mmol) was added cautiously. The reaction mixture was worked-up with 20% NaOH and refluxed for 5 h. The organic layer was separated, and the aqueous layer was extracted with ether (3×20 mL). According to GLC data, the ethereal solution contained 94% of amine **4b** and 6% of 1-butylisoquinoline. Ether (50 mL) and 5 *N* HCl (5.7 mL) were added to the solution of these compounds. The resulting water-insoluble salt **4b** · HCl was filtered off and recrystallized from an ether—MeOH mixture. A 20% NaOH solution (15 mL) was added to the salt obtained (10 g, 74% with respect to isoquinoline), and the mixture was refluxed until complete dehydrochlorination. The aqueous layer was extracted with ether, and the extract was dried with K_2CO_3. The solvents were concentrated *in vacuo*. Distillation of the residue gave 7.06 g (60% with respect to isoquinoline) of amine **4b**, b.p. 131—132 °C (1 Torr), n_D^{19} 1.5251. IR (pure compound), ν/cm^{-1}: 3300 (br), 3080, 3020, 2930, 2870, 1640, 1580, 1490, 1455, 1380, 1330, 1140, 1110, 1045, 1000, 920, 745, 675. ^{1}H NMR (400 MHz), δ: 0.91 (t, 3 H, CH_3); 1.34 (m, 4 H, $CH_2\underline{CH_2}\underline{CH_2}Me$); 1.53 (m, 1 H, $\underline{CH_b}HPr$); 1.69 (m, 2 H, NH and $\underline{CH_a}HPr$); 2.11 (m, 1 H, H_a(3′)); 2.16 (m, 1 H, H_b(3′)); 2.38 (dd, 1 H, H_a(4), ^2J = 16.2 Hz, ^3J = 10.2 Hz); 2.61 (dd, 1 H, H_b(4), ^2J = 16.2 Hz, ^3J = 3.9 Hz); 2.99 (m, 1 H, H(3)); 3.83 (dd, 1 H, H(1), ^3J = 10.3 Hz, 3.8 Hz); 5.05 (dd, 1 H, H_a(5′), ^3J = 10.2 Hz, ^2J = 2 Hz); 5.09 (dd, 1 H, H_b(5′), ^3J = 15.7 Hz, ^2J = 2 Hz); 5.79 (m, 1 H, H(4′)); 6.94 (m, 2 H, Ph); 7.00 (m, 2 H, Ph). ^{13}C NMR, δ: 13.61 (CH_3); 22.08 ($C_2H_4\underline{C}H_2Me$); 28.48 ($CH_2\underline{C}H_2Et$); 35.17 (C(4)); 35.88 ($\underline{C}H_2Pr$); 40.48 (C(3′)); 45.62 (C(3)); 54.97 (C(1)); 116.71 (C(5′)); 124.90, 125.23, 126.17 (C(5), C(6), C(7)); 128.48 (C(8)); 133.77 (C(4a)); 134.91 (C(4′)); 139.40 (C(8a)). MS, *m/z*: 229 [M]$^+$, 188 [M−C_3H_5]$^+$, 172 [M−C_4H_9]$^+$, 130 [M−(C_4H_9+CH_2=CH−CH_3)]$^+$.

***trans*-3-Allyl-1-butyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (4b · HCl).** M.p. 165.5—167 °C (from an ether—MeOH mixture). Found (%): C, 71.91; H, 9.16; N, 5.32; Cl, 13.49. $C_{16}H_{23}N$ · HCl. Calculated (%): C, 72.29; H, 9.10; N, 5.27; Cl, 13.34. IR (pellets with KBr), ν/cm^{-1}: 3420 (br), 2940, 2960, 2620, 2470, 1600, 1495, 1460, 1430, 1380, 1000, 930, 770, 760, 745, 440. ^{1}H NMR (400 MHz), δ: 0.92 (t, 3 H, CH_3); 1.41 (m, 2 H, $C_2H_4\underline{CH_2}Me$); 1.59 (m, 2 H, $CH_2\underline{CH_2}Et$); 1.99 (m, 1 H, $\underline{CH_b}HPr$); 2.24 (m, 1 H, $\underline{CH_a}HPr$); 2.52 (m, 1 H, H_a(3′)); 3.08 (m, 2 H, H_b(3′), H_a(4)); 3.19 (dd, 1 H, H_b(4), ^2J = 17.2 Hz, ^3J = 4.8 Hz); 3.73 (m, 1 H, H(3)); 4.52 (dd, 1 H, H(1), ^3J = 6.3 Hz, 6.2 Hz); 5.19 (m, 1 H, H_a(5′)); 5.21 (m, 1 H, H_b(5′)); 5.84 (m, 1 H, H(4′)); 7.12 (m, 2 H, Ph); 7.23 (m, 2 H, Ph); 9.79 (br.s, 1 H, NH); 10.31 (br.s, 1 H, NH). ^{13}C NMR, δ: 13.50 (CH_3); 22.19 ($C_2H_4\underline{C}H_2Me$); 27.59 ($CH_2\underline{C}H_2Et$); 30.25 (C(4)); 34.26 ($\underline{C}H_2Pr$); 35.66 (C(3′)); 49.23 (C(3)); 53.84 (C(1)); 119.28 (C(5′)); 126.29, 126.44, 127.52 (C(5), C(6), C(7)); 129.05 (C(8)); 130.34 (C(4a)); 131.71 (C(4′), C(8a)).

***trans*-3-Allyl-1-phenyl-1,2,3,4-tetrahydroisoquinoline (4c).** A solution of isoquinoline in anhydrous ether (25 mL) was added at −15 °C to a 1.3 *N* solution of PhLi (15.2 mL, 19.7 mmol) in ether. The mixture was stirred for 1 h at 10 °C, and triallylborane (2.64 g, 19.7 mmol) was then added at −30 °C. The solution temperature was brought to 0 °C (in 1 h), and anhydrous MeOH (3.2 mL, 79 mmol) was cautiously added at −30 °C. The reaction mixture was worked up at 20 °C with a 20% solution of NaOH (8.5 mL) and refluxed for 1 h. The organic layer was separated; the aqueous layer was extracted with ether (3×8 mL), and the extract was dried with K_2CO_3. The solvents were evaporated *in vacuo*; distillation of the residue gave 2.68 g (55%) of amine **4c**, b.p. 160—162 °C (1 Torr), n_D^{19} 1.5896. IR (pure compound), ν/cm^{-1}: 3320 (br), 3060, 3020, 2970, 2910, 2830, 1640, 1595, 1580, 1490, 1450, 1310, 1120, 1075, 1030, 1000, 920, 840, 790, 740, 705, 600, 575, 440. ^{1}H NMR (400 MHz), δ: 2.31 (m, 3 H, H(3′), NH); 2.77 (dd, 1 H, H_a(4), ^2J = 16.3 Hz, ^3J = 9.6 Hz); 3.03 (dd, 1 H, H_b(4), ^2J = 16.3 Hz, ^3J = 4.1 Hz); 3.22 (m, 1 H, H(3)); 5.14 (m, 1 H, H_a(5′)); 5.17 (m, 1 H, H_b(5′)); 5.38 (s, 1 H, H(1)); 5.80 (m, 1 H, H(4′)); 7.05 (m, 1 H, Ph); 7.13—7.40 (m, 8 H, Ar). ^{13}C NMR, δ: 35.03 (C(4)); 40.16 (C(3′)); 46.13 (C(3)); 59.45 (C(1)); 117.14 (C(5′)); 125.38, 126.28, 126.73, 127.97, 128.29, 128.84 (C_o, C_m, C_p, C(5), C(6), C(7), C(8)); 134.79 (C(4′)); 135.14 (C(4a)); 136.11 (C_i); 145.30 (C(8a)). MS, *m/z* (I_{rel} (%)): 249 [M$^+$] (2), 208 [M−C_3H_5]$^+$ (100), 179 [M−(C_3H_5+CH_2=NH)]$^+$ (16), 165

$[M-(C_5H_5+C_2H_5N)]^+$ (18.5), 130 $[M-(C_5H_5+C_6H_6)]^+$ (70), 103 $[M-(C_5H_5+C_6H_6+HCN)]^+$ (12), 91 $[C_7H_7]^+$ (12.5).

***trans*-3-Allyl-1-phenyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (4c · HCl)** was obtained by treatment of amine **4c** with an ethereal solution of HCl, yield 86%, m.p. 211.5—212.5 °C (from an ether—MeOH mixture). Found (%): C, 75.44; H, 7.09; N, 5.11; Cl, 12.55. $C_{18}H_{19}N \cdot HCl$. Calculated (%): C, 75.64; H, 7.05; N, 4.90; Cl, 12.42. IR (pellets with KBr), ν/cm^{-1}: 3420 (br), 2850, 2820,1650, 2590, 2510, 2470, 1640, 1590, 1490, 1470, 1455, 1430, 1290, 1010, 990, 930, 785, 750, 700, 645, 610, 570, 440, 410. ^{1}H NMR (400 MHz), δ: 2.42 (m, 1 H, $H_a(3')$); 2.86 (m, 1 H, $H_b(3')$); 3.12 (dd, 1 H, $H_a(4)$, ^2J = 17.3 Hz, ^3J = 8.6 Hz); 3.25 (dd, 1 H, $H_b(4)$, ^2J = 17.3 Hz, ^3J = 4.6 Hz); 3.50 (m, 1 H, H(3)); 5.08 (m, 1 H, $H_a(5')$); 5.11 (m, 1 H, $H_b(5')$); 5.52 (m, 1 H, H(1)); 5.67 (m, 1 H, H(4')); 6.83 (m, 1 H, Ph); 7.14 (m, 2 H, Ar); 7.25 (m, 1 H, Ar); 7.33 (m, 5 H, Ar); 9.77 (m, 1 H, NH); 10.81 (m, 1 H, NH). ^{13}C NMR, δ: 30.14 (C(4)); 35.42 (C(3')); 48.91 (C(3)); 57.29 (C(1)); 119.35 (C(5')); 126.76, 127.91, 128.11, 128.62, 129.0, 129.25, 130.34, 130.64, 131.58 (Ar); 131.80 (C(4')); 136.09 (C(8a)).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32555) and the Council on Grants and Support of Leading Scientific Schools of the President of the Russian Federation (Grant No. 96-15-97289).

References

1. Yu. N. Bubnov, S. V. Evchenko, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1325 [*Russ. Chem. Bull.*, 1993, **42**, 1268 (Engl. Transl.)].
2. Yu. N. Bubnov, *Pure Appl. Chem.*, 1994, **66**, 235.
3. Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1203 [*Russ. Chem. Bull.*, 1995, **44**, 1156 (Engl. Transl.)].
4. Yu. N. Bubnov, E. V. Klimkina, A. V. Ignatenko, and I. D. Gridnev, *Tetrahedron Lett.*, 1996, **37**, 1337.
5. Yu. N. Bubnov, E. V. Klimkina, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 467 [*Russ. Chem. Bull.*, 1998, **46**, 451 (Engl. Transl.)].
6. Yu. N. Bubnov, E. V. Klimkina, A. V. Ignatenko, and I. D. Gridnev, *Tetrahedron Lett.*, 1997, **38**, 4631.
7. K. Ziegler and H. Zeiser, *Lieb. Ann. Chem.*, 1931, **485**, 174.
8. P. A. Clare, in *Comprehensive Organic Chemistry*, Eds. D. Barton and W. D. Ollis, Pergamon Press, Oxford—New York—Toronto—Sydney—Paris—Frankfurt, 1979, **4**, Ch. 16.5.
9. Yu. N. Bubnov, A. Yu. Zykov, A. V. Ignatenko, A. G. Mikhailovskii, Yu. V. Shklyaev, and V. S. Shklyaev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 935 [*Russ. Chem. Bull.*, 1996, **45**, 890 (Engl. Transl.)].
10. Yu. N. Bubnov, M. E. Gurskii, and T. V. Potapova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2807 [*Russ. Chem. Bull.*, 1996, **45**, 2665 (Engl. Transl.)].

Received November 19, 1997;
in revised form December 11, 1997