Reductive mono- and diallylation of the bis(pyridine)dihydropyridyllithium dimer by triallylborane

Yu. N. Bubnov,[a,b]★ E. V. Klimkina,[a] Z. A. Starikova,[b] and A. V. Ignatenko[a]

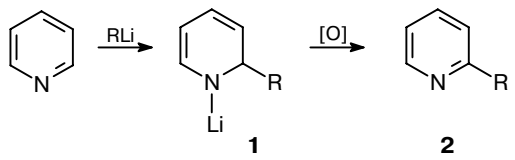
[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: bor@cacr.ioc.ac.ru
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: dir@ineos.ac.ru

Reductive allylation of the bis(pyridine)dihydropyridyllithium dimer containing the 1,2- and 1,4-dihydropyridine fragments by triallylborane results mainly in *trans*- and *cis*-2,6-diallylpiperidines (60—85%), their ratio depending on the nature of the solvent. The minor reactions products are 2-allyl-1,2,3,6-tetrahydropyridine and 4,10-diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane. The unexpected formation of the latter is due to hetero-Diels—Alder condensation of intermediate products formed in the allylboration of dihydropyridines. The stereochemistry of *trans*- and *cis*-2,6-diallylpiperidines was determined from the ^{1}H and ^{13}C NMR spectra of the respective *N*,*N*-dimethylpiperidinium iodides. The structure of 4,10-diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane dipicrate was established by X-ray diffraction analysis.

Key words: pyridine, reaction with butyllithium, bis(pyridine)dihydropyridyllithium dimer; allylboration; 2-allyl-1,2,3,6-tetrahydropyridine; *trans*- and *cis*-2,6-diallylpiperidines, *N*,*N*-dimethylpiperidinium iodides, stereochemistry; 4,10-diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane, the hetero-Diels—Alder reaction, X-ray diffraction analysis.

In 1930, it was shown[1] for the first time that organolithium compounds react with pyridine to give 1,2-addition products **1**, whose aromatization results in 2-R-pyridines (Scheme 1).

Scheme 1

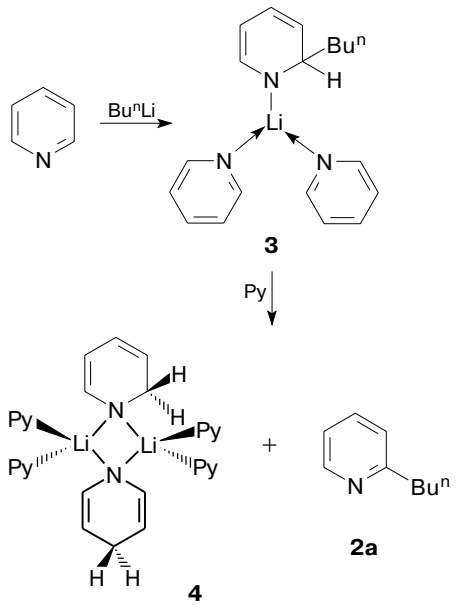


1 **2**

Later, this reaction was used by many chemists to obtain 2-substituted pyridines.[2] However, it has been recently found that this process (substitution of the α-hydrogen atom) proceeds through intermediate adduct of the type **3** (Scheme 2).[3,4] When treated with 4 equiv. of pyridine, the latter gave 2-butylpyridine **2a** and an air-stable bis(pyridine)dihydropyridyllithium dimer (**4**), which contains the 1,2- and 1,4-dihydropyridyllithium fragments (in the ratio 1 : 1) and four pyridine molecules.[5]

Formally, the reaction involving adduct **3** includes the reduction of pyridine with lithium hydride generated in the formation of 2-butylpyridine. However, lithium hydride has not been detected in the reaction products. The data obtained[5] indicate that 2-alkylpyridine results

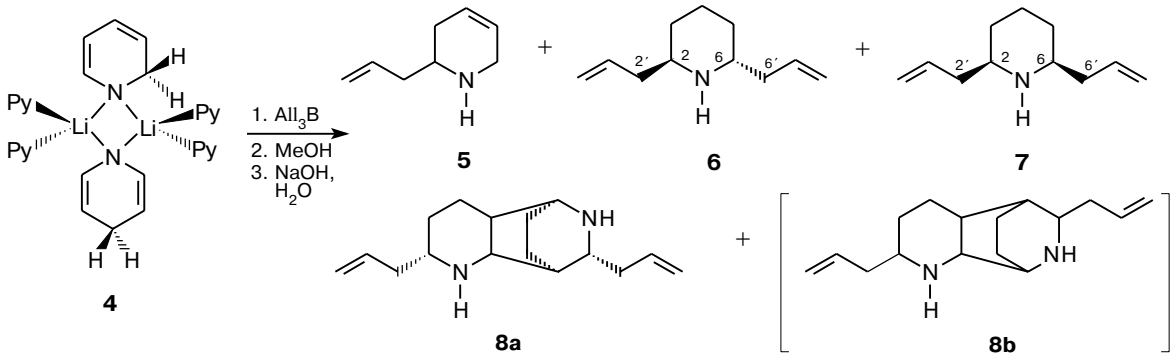
Scheme 2



3 **4** **2a**

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1032—1037, June, 2001.

Scheme 3



from the reaction of adduct **3** with pyridine. These data also explain the formation of 2-alkylpyridines as by-products in the synthesis of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines from pyridine, RLi, and triallylborane.[6]

Both dihydropyridine fragments of dimer **4** are attractive objects for the reductive allylboration studied by us earlier.[6,7] We believed that monoallylated compound **5** can be obtained by the reductive allylation of complex **4** (Scheme 3) and further transformed into 2-propylpiperidine (the alkaloid coniine).

However, it turned out that consecutive treatment of complex **4** with triallylborane, methanol, and alkali (one-pot procedure) gives a mixture of the allylation products, namely, 2-allyl-1,2,3,6-tetrahydropyridine **5**, *trans*- and *cis*-2,6-diallylpiperidines (**6** and **7**, respectively), tricyclic compound **8a**, and probably its isomer **8b** (see Scheme 3).

Solid complex **4** (prepared from pyridine and *n*-butyllithium according to the known procedure[5]) was initially washed with hexane to separate 2-butylpyridine. Then, a solvent (THF or ether) was added. The reaction mixture was cooled to −40 °C, and triallylborane and methanol were added. The resulting aminoboranes were deboronated with 20% NaOH.

The ratio of products **5**—**8** depends on the solvent used (Table 1).

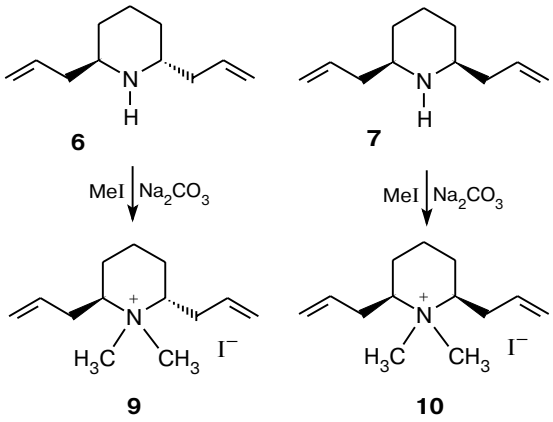
Solvent	Y (%)*				
	5	**6**	**7**	**8a**	**8b**
THF	15	35	25	20	~3
Et_2O	10	50	35	4	<1

* The yield of the final products (Y) was determined from the ^{13}C NMR spectra.

A mixture of the reaction products was distilled and chromatographed to give individual amine **5**, *trans*-piperidine **6**, and *cis*-piperidine **7**. A mixture of tricyclic compounds **8a** and **8b** purified by chromatography was treated with picric acid. Recrystallization from ethanol gave individual bispicrate **8a · 2Pic**.

To determine the configuration of diallylpiperidines **6** and **7**, we synthesized methiodides of the corresponding *N*-methyl derivatives **9** (71%) and **10** (67%) (Scheme 4).

Scheme 4

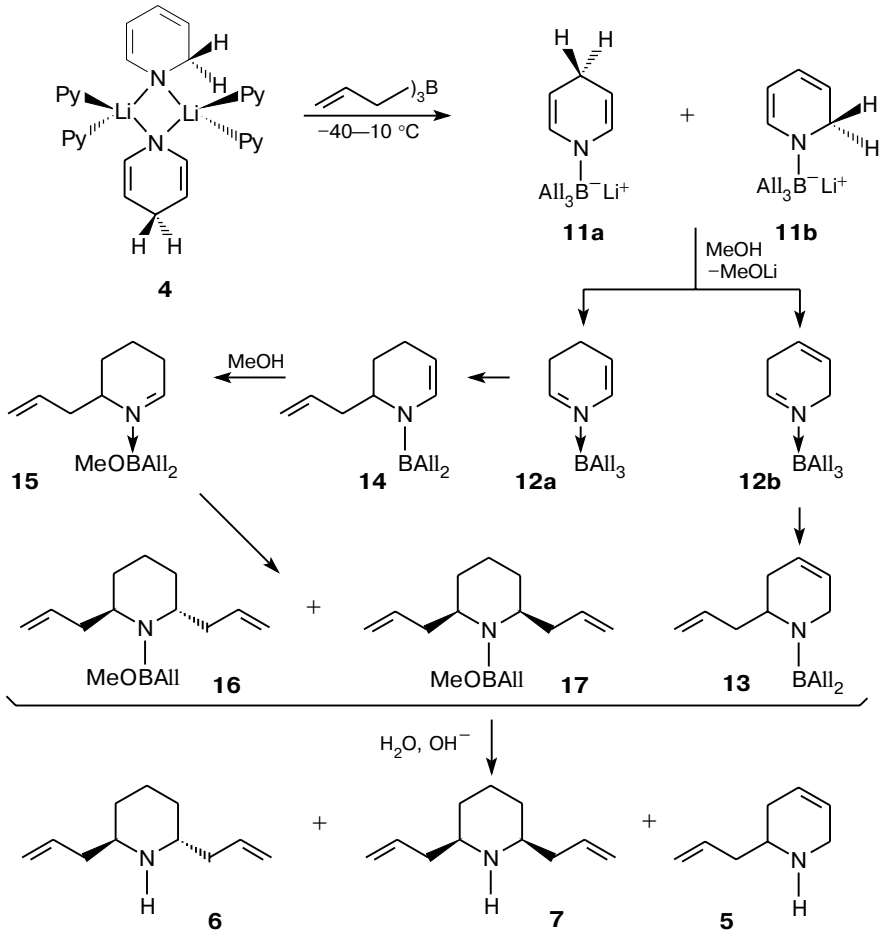


In salt **9**, both methyl groups are equivalent, giving one signal in both ^1H (δ 3.17, 6 H) and ^{13}C NMR spectra (δ 48.85). A similar spectral pattern was observed earlier for *N*,*N*-dimethyl-*trans*-2,6-dimethylpiperidinium iodide[8] and *N*,*N*-dimethyl-*trans*-2,6-dipropylpiperidinium iodide.[6] These data indicate unambiguously that the allyl groups in amine **6** are *trans*-arranged. The methyl groups in salt **10** are nonequivalent, producing two singlets at δ 2.56 and 3.12 in the ^1H NMR spectrum and two signals at δ 37.66 and 49.04 in the ^{13}C NMR spectrum, which confirms the *cis*-arrangement of the substituents in piperidine **7**. A similar pattern was observed earlier for *cis*-1,1,2,6-tetramethylpiperidinium iodide[8] and *cis*-1,1-dimethyl-2,6-dipropylpiperidinium iodide.[6] The signals in the NMR spectra of compound **5** were assigned using ^1H—^1H COSY-45 spectra.

Amines **5**—**7** were converted into hydrochlorides **5**—**7 · HCl**. The possible mechanism for the formation of compounds **5**—**7** is shown in Scheme 5.

The reaction of complex **4** with triallylborane yields a mixture of two enamino complexes **11a**,**b** with differ-

Scheme 5



ent positions of the double bonds in the ring. Methanolysis of these complexes (cleavage of the B—N bond) is accompanied by the allyl-type rearrangement to give a mixture of imino adducts **12a**,**b**. Rapid allylboration of their C=N bonds results in monoallylated aminoborane **13** and enaminoborane **14**. When treated with methanol, the latter gives a new imino complex **15**, which is transformed, through a six-membered transition state, into aminoboranes **16** and **17**. Subsequent alcoholysis of aminoboranes **13**, **16**, and **17** affords monoallylated 3-piperideine **5** and two diallylated piperidines **6** and **7**.

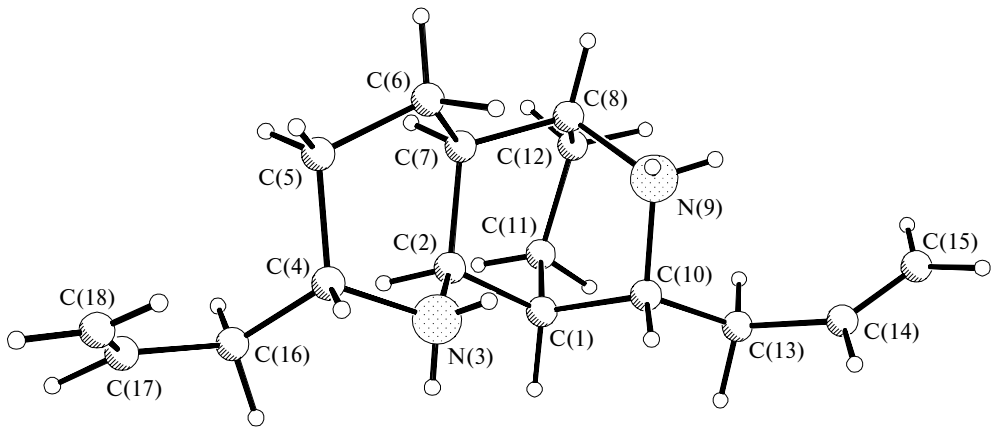


Fig. 1. Structure of the dication in compound **8a · 2Pic**.

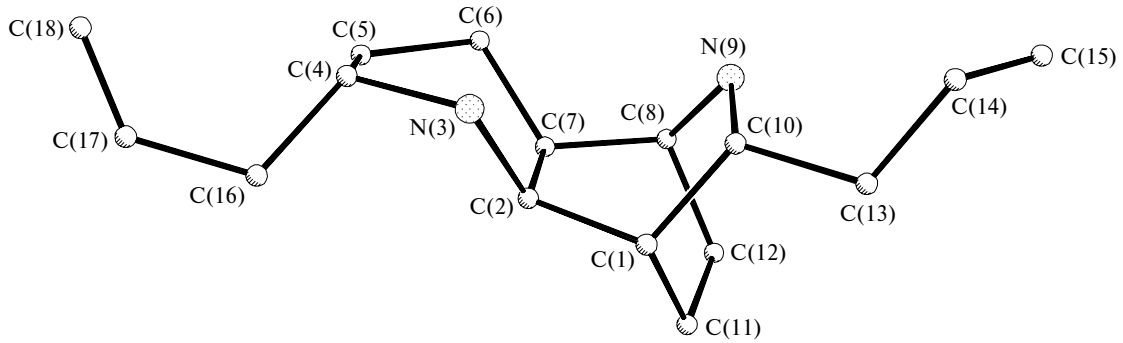
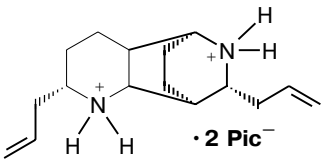


Fig. 2. General view of dication **8a** of picrate **8a · 2Pic** (the hydrogen atoms are not displayed).

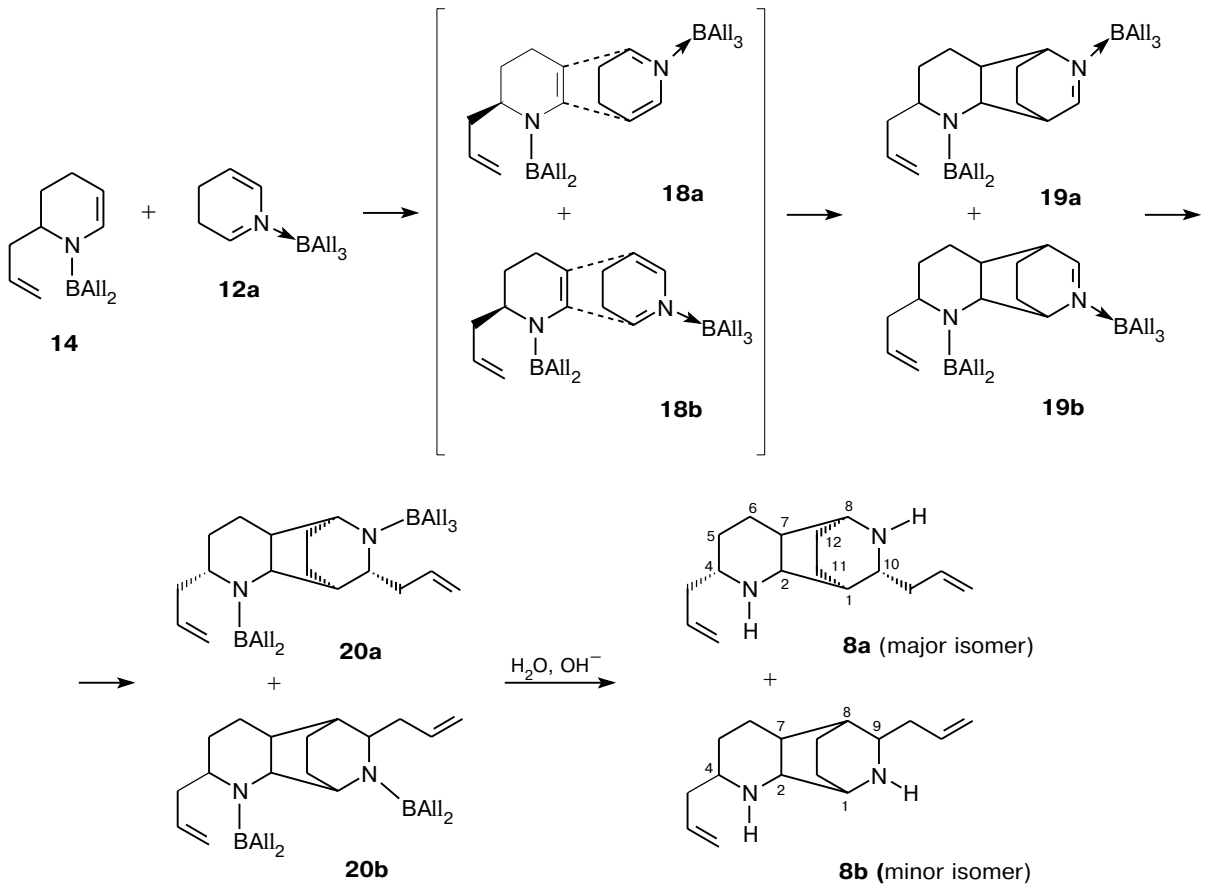
The structure of tricyclic compound **8a** (4,10-diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane) was determined by the X-ray diffraction analysis of its dipicrate (Figs. 1 and 2).



Crystal **8a · 2Pic** is composed of the tricyclic dication and two picrate anions. In addition, the structure contains a disordered molecule of a solvent (hexane).

The dication is built from the N(3)C(4)C(5)C(6)C(7)C(2) and N(9)C(10)C(1)C(2)C(7)C(8) piperidine heterocycles fused along the C(2)—C(7) bond. Each heterocycle has a boat conformation. In the former ring, the C(2)C(4)C(5)C(7) atoms are coplanar (plane *1*) (the

Scheme 6



standard deviation is ±0.087 Å), while the N(3) and C(6) atoms deviate from this plane by 0.650(3) Å. In the latter ring, the C(2)C(7)N(9)C(10) atoms are coplanar (plane *2*) (the standard deviation is ±0.063 Å), while the C(1) and C(8) atoms deviate from this plane by 0.690(3) Å. Planes *1* and *2* make a dihedral angle of 55.3(1)° (see Fig. 2).

The C(16)C(17)C(18) allyl group is pseudoaxial relative to the N(3)C(4)C(5)C(6)C(7)C(2) piperidine ring, while the C(13)C(14)C(15) allyl group is in the pseudoequatorial position relative to the N(9)C(10)C(1)C(2)C(7)C(8) ring. The orientation of these allyl groups is characterized by the following torsion angles:
N(3)—C(4)—C(16)—C(17) 157.5(2)°,
C(1)—C(10)—C(13)—C(14) 174.1(2)°,
C(4)—C(16)—C(17)—C(18) 10.9(4)°,
N(9)—C(10)—C(13)—C(14) 64.3(3)°,
C(5)—C(4)—C(16)—C(17) 80.4(4)°,
C(10)—C(13)—C(14)—C(15) 119.4(4)°.

The cations and anions in molecule **8a · 2Pic** are held together by hydrogen bonds involving the protonated N atoms and the deprotonated O atoms of picrate: N(3)—H(31)O(1) (HO 2.02(3) Å), N(3)—H(32)O(1) (HO 1.86(3) Å), N(9)—H(92)O(1) (HO 1.88(3) Å). One of the nitro groups of the anion is also involved in hydrogen bonding (N(9)—H(91)O(7) (HO 2.24(3) Å)).

The signals in the ^{1}H NMR spectra of picrate **8a · 2Pic** were assigned using ^{1}H—^{1}H COSY spectra (see Experimental).

The formation of compounds **8a**,**b** can be explained by the hetero-Diels—Alder condensation of imino complex **12a** (diene component) with enamine **14** (Scheme 6).

Apparently, the condensation proceeds through transition states **18a** (major pathway) and **18b** (minor pathway) to give two tricyclic imino complexes **19a**,**b**. The C=N bond in these complexes is allylborated from the least hindered side, yielding a mixture of two aminoboranes **20a**,**b**. Their alcoholysis results in the formation of tricyclic compounds **8a**,**b** differing in the mutual arrangement of the allyl groups and in the position of the NH fragment in the polycycles (9 and 10, respectively).

Thus, in this work, allylboration of 1,2- and 1,4-dihydropyridines generated from pyridine by the action of butyllithium was carried out for the first time. The main products of this complex reaction are *trans*- and *cis*-2,6-diallylpiperidines, 2-allyl-1,2,3,6-tetrahydropyridine, and 4,10-diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane.

The data obtained are of fundamental importance for understanding the mechanism of the reductive mono- and *trans*-diallylation of aromatic nitrogenous heterocycles by allylboranes.[9,10] The unexpected formation of tricyclic compound **8a** with the fixed orientation of two allyl groups is yet another important result of this study. Such heterocyclic systems are difficult to obtain by other methods.

Experimental

All manipulations with organoboron and organolithium compounds were carried out in an atmosphere of dry argon. Triallylborane[11] and *n*-butyllithium[12] were prepared according to known procedures.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer. ^{1}H—^{1}H COSY spectra were recorded on a Bruker AMX-400 instrument; the chemical shifts are given on the δ scale and referenced to $SiMe_4$. Mass spectra (EI) were obtained with the Kratos MS-30 spectrometer (70 eV). X-Ray diffraction analysis was carried out on a Siemens P3/PC diffractometer at −120 °C.

Synthesis of 2-allyl-1,2,3,6-tetrahydropyridine (5), *trans*-2,6-diallylpiperidine (6), *cis*-2,6-diallylpiperidine (7), and tricyclic compounds (8a,b). A solution of pyridine (21.12 g, 21.5 mL, 267 mmol) in 20 mL of anhydrous hexane was placed in a three-necked flask equipped with a reflux condenser, a thermometer, a dropping funnel, and an inlet for argon. Addition of 1.78 *M* Bu^{n}Li (50 mL, 89 mmol) in hexane at −30 °C gave complex **3** as an orange precipitate. The reaction mixture was stirred at ~30—40 °C until the precipitate dissolved completely. Then pyridine (28.16 g, 28.63 mL, 356 mmol) was added, and the solution was kept without stirring at 50 °C (in a water bath) for 3 h and left overnight. The crystalline precipitate of complex **4** was separated by decantation and washed with anhydrous hexane (3×30 mL). After the addition of anhydrous THF (50 mL), complex **4** was cooled to −40 °C, and triallylborane (11.92 g, 15.5 mL, 89 mmol) was carefully added. The reaction mixture was stirred at 20 °C until the precipitate completely dissolved. Anhydrous MeOH (15 mL, 371 mmol) at −40 °C and then 20% NaOH (35 mL) at 10 °C were added, and the resulting mixture was refluxed for 2 h. The products were extracted with ether, and the organic extracts were dried with K_2CO_3. After the removal of the solvents at atmospheric pressure, the reaction mixture contained piperideine **5** (15%), *trans*-piperidine **6** (35%), *cis*-piperidine **7** (25%), tricyclic compound **8a** (20%), and its isomer **8b** (3%) (^{13}C NMR data). Distillation gave three fractions: fraction *1*, b.p. 70—90 °C (20 Torr); fraction *2*, b.p. 50—90 °C (1 Torr), and fraction *3*, b.p. 90—120 °C (1 Torr). Fraction *1* was purified by column chromatography on Al_2O_3 in hexane—ether (5 : 1) and distilled to give amine **5** (0.94 g, 8.6%), b.p. 68—69 °C (19 Torr). Column chromatography of fraction *2* on Al_2O_3 in hexane—ether (10 : 1) followed by distillation gave *trans*-amine **6** (1.95 g, 13.3%), b.p. 100—101 °C (19 Torr) and *cis*-amine **7** (1.37 g, 9.3%), b.p. 93—94 °C (19 Torr). Column chromatography of fraction *3* (Al_2O_3, ether) afforded tricyclic compound **8a** (1.48 g, 6.8%), b.p. 107—109 °C (1 Torr), with an admixture of isomer **8b** (~10%).

2-Allyl-1,2,3,6-tetrahydropyridine (5): n_D^{19} 1.4842. MS, *m/z* (I_{rel} (%)): 122 $[M - H]^+$ (24%), 96 $[M - C_2H_3]^+$ (48%), 82 $[M - C_3H_5]^+$ (100%), 70 $[C_4H_5]^+$ (29%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.70—2.35 (m, 5 H, C—CH_2—C, NH); 2.65—2.90 (m, 1 H, H(2)); 3.25−3.55 (m, 2 H, NCH_2); 4.95—5.25 (m, 2 H, CH_2=); 5.55—5.95 (m, 3 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 31.3 (C(3)), 40.5 (C(2′)), 44.8 (C(2)), 51.3 (C(6)), 116.7 (CH_2=), 124.5 (C(4)), 125.8 (C(5)), 134.7 (C(3′)).

***trans*-2,6-Diallylpiperidine (6)**: n_D^{19} 1.4783. MS, *m/z* (I_{rel} (%)): 164 $[M - H]^+$ (4%), 124 $[M - C_3H_5]^+$ (100%),

82 [M − C_3H_5 − C_3H_6]$^+$ (68%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.20—1.45 (m, 2 H, H(4)); 1.50—1.75 (m, 4 H, H(3), H(5)); 1.80—2.00 (br.s, 1 H, NH); 2.00—2.30 (m, 4 H, —CH_2— in All); 2.85−3.00 (m, 2 H, NCH); 4.90—5.20 (m, 4 H, CH_2=); 5.60—5.85 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 19.3 (C(4)), 30.3 (C(3), C(5)), 38.4 (C(2′), C(6′)), 49.4 (NCH), 116.6 (CH_2=), 135.4 (—CH=).

***cis*-2,6-Diallylpiperidine (7)**: n_D^{19} 1.4739. MS, *m/z* (I_{rel} (%)): 164 [M − H]$^+$ (4%), 124 [M − C_3H_5]$^+$ (100%), 82 [M − C_3H_5 − C_3H_6]$^+$ (58%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.80—1.45 (m, 3 H, H(4), NH); 1.50—2.30 (m, 8 H, H(3), H(5), —CH_2— in All); 2.30−2.60 (m, 2 H, NCH); 4.90—5.25 (m, 4 H, CH_2=); 5.50—5.90 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 24.3 (C(4)), 32.0 (C(3), C(5)), 41.2 (C(2′), C(6′)), 55.6 (NCH), 116.7 (CH_2=), 135.0 (—CH=).

4,10-Diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane (8a): n_D^{19} 1.5267. MS, *m/z* (I_{rel} (%)): 246 [M]$^+$ (5%), 205 [M − C_3H_5]$^+$ (26%), 124 [M/2 + H]$^+$ (47%), 123 [M/2]$^+$ (14%), 122 [M/2 − H]$^+$ (52%), 82 [M/2 − C_3H_5]$^+$ (100%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.05—2.45 (m, 16 H); 3.00—3.55 (m, 4 H, NCH); 4.95—5.30 (m, 4 H, CH_2=); 5.60—6.00 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 18.9, 21.4 (C(6), C(11)), 28.1, 28.3 (C(5), C(12)), 33.7 (C(1)), 39.1 (C(7)), 40.8, 40.9 (—CH_2— in All), 48.1, 48.4, 48.9, 50.2 (NCH), 115.7, 116.3 (CH_2= in All), 136.0, 136.2 (CH_2= in All).

2-Allyl-1,2,3,6-tetrahydropyridine hydrochloride (5 · HCl) was prepared by the treatment of amine **5** with ethereal HCl, m.p. 142—143 °C (from ether—MeOH). Found (%): C, 60.09; H, 9.06; Cl, 22.54. $C_8H_{14}ClN$. Calculated (%): C, 60.18; H, 8.84; Cl, 22.21. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.35 (m, 2 H, H(3)); 2.47 (m, 1 H, H_a(2′)); 2.81 (m, 1 H, H_b(2′)); 3.15 (m, 1 H, NCH); 3.66 (m, 2 H, NCH_2); 5.12 (m, 2 H, CH_2=); 5.57—5.74 (m, 2 H, H(4), —CH= in All); 5.79 (m, 1 H, H(5)); 9.64 (br.s, 1 H, NH); 9.76 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 26.8 (C(3)), 36.6 (C(2′)), 41.7 (C(2)), 52.1 (C(6)), 119.5, 119.7 (C(4), CH_2=), 125.1 (C(5)), 131.3 (C(3′)).

***trans*-2,6-Diallylpiperidine hydrochloride (6 · HCl)** was prepared analogously from amine **6**, m.p. 190—192 °C (from ether—MeOH). Found (%): C, 65.17; H, 10.15; Cl, 17.66. $C_{11}H_{20}ClN$. Calculated (%): C, 65.49; H, 10.0; Cl, 17.57. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.55—1.85 (m, 4 H, H_a(3), H_a(5), H(4)); 1.85—2.20 (m, 2 H, H_b(3), H_b(5)); 2.35—2.70 (m, 2 H, H_a(2′), H_a(6′)); 2.75−3.10 (m, 2 H, H_b(2′), H_b(6′)); 3.30—3.60 (m, 2 H, NCH); 5.10—5.45 (m, 4 H, CH_2=); 5.55—6.00 (m, 2 H, —CH=); 9.45 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 16.9 (C(4)), 25.4 (C(3), C(5)), 34.9 (C(2′), C(6′)), 51.5 (NCH), 119.2 (CH_2=), 132.0 (—CH=).

***cis*-2,6-Diallylpiperidine hydrochloride (7 · HCl)** was prepared analogously from amine **7**, m.p. 247—248.5 °C (from ether—MeOH). Found (%): C, 65.18; H, 10.14; Cl, 17.44. $C_{11}H_{20}ClN$. Calculated (%): C, 65.49; H, 10.00; Cl, 17.57. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.20—2.10 (m, 6 H, H(3), H(4), H(5)); 2.40—2.70 (m, 2 H, H_a(2′), H_a(6′)); 2.80−3.20 (m, 4 H, H_b(2′), H_a(6′), NCH); 5.00—5.45 (m, 4 H, CH_2=); 5.55—5.95 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 22.7 (C(4)), 27.9 (C(3), C(5)), 37.8 (C(2′), C(6′)), 58.0 (NCH), 119.1 (CH_2=), 132.3 (—CH=).

4,10-Diallyl-3,9-diazatricyclo[6.2.2.0^{2,7}]dodecane picrate (8a · 2Pic). A solution of picric acid (0.39 g, 1.7 mmol) in EtOH was added to a solution of tricyclic compound **8a** in 10 mL of anhydrous hexane (0.21 g, 0.85 mmol). The resulting solution was stirred for 2 h and concentrated *in vacuo*. Crystallization from EtOH lasted for 10 days and gave crystals of picrate **8a · 2Pic**, m.p. 175—185 °C (decomp.). Found (%): C, 47.87; H, 4.64. $C_{28}H_{32}N_8O_{14}$. Calculated (%): C, 47.73; H, 4.58. ^{1}H NMR (400 MHz, CD_3COCD_3), δ: 1.61 (m, 1 H, H_a(12)); 1.92 (m, 3 H); 2.22 (m, 3 H); 2.36 (m, 1 H, H_a(11)); 2.55—2.85 (m, 6 H); 3.67 (m, 1 H, H(2)); 3.94 (m, 1 H, H(8)); 4.22 (m, 2 H, H(4), H(10)); 4.98—5.24 (m, 4 H, CH_2=); 5.66 (m, 1 H, —CH=); 5.80 (m, 1 H, —CH=); 8.74 (s, 4 H, CH—CNO_2); 9.00 (br.s, 4 H, NH). ^{13}C NMR (DMSO), δ: 16.6, 19.5 (C(6), C(11)), 21.7, 24.0 (C(5), C(12)), 29.3, 32.7 (C(1), C(7)), 34.6, 37.1 (—CH_2— in All), 48.1, 48.3, 48.8, 50.1 (NCH), 119.2, 119.3 (CH_2= in All), 124.8 (C_m), 125.4 (C_O), 132.6, 132.9 (—CH= in All), 141.8 (C_p), 161.0 (C—NO_2). The single crystal of picrate **8a · 2Pic** was obtained by crystallization from hexane—EtOH.

X-ray diffraction analysis of 8a · 2Pic: The crystals of **8a · 2Pic 0.5C_6H_{14}** are triclinic, M = 747.70, [$C_{31}H_{39}N_8O_{14}$], space group $P\bar{1}$, Z = 2, at 153 K a = 8.306(2), b = 10.998(3), c = 20.619(7) Å, α = 87.46(3)°, β = 80.03(3)°, γ = 69.93(2)°, V = 1742.1(9) Å^3, d_{calc} = 1.425 g cm^{-3}. The unit cell parameters and the intensities of 6831 reflections were obtained on a Siemens P3/PC diffractometer (molybdenum radiation, graphite monochromator, θ/2θ scan mode, 2θ > 54°). The equivalent reflections were averaged to give 6158 independent reflections. The structure was solved by the direct method and refined on F^2_{hkl} by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The H atoms were located from the electron density difference maps and refined isotropically, except for the hydrogen atoms in the C_{14}=C_{15} allyl group, which were refined in the "riding" model with the thermal factors U_{eq}(H) = 1.2 U_{eq}(C). The final discrepancy factors are R_1 = 0.0548 (on F_{hkl} for 4808 reflections with $I > 2\sigma(I)$), R_w2 = 0.1925 (on F^2_{hkl} for all reflections included in the refinement of 611 independent parameters). All calculations were performed on an IBM-PC/AT with the SHELXTL PLUS program.[13] Complete tables of the bond lengths and angles, atomic coordinates, and thermal parameters have been deposited with the Cambridge Crystallographic Database.

***trans*-2,6-Diallyl-1,1-dimethylpiperidinium iodide (9).** A mixture of amine **6** (0.4 g, 2.4 mmol), MeI (0.3 mL, 4.8 mmol), and K_2CO_3 (0.67 g, 4.8 mmol) in 5 mL of EtOH was refluxed for 5 h. The precipitate that formed was filtered off, and the filtrate was concentrated *in vacuo*. The products were extracted with chloroform, and the extract was filtered and concentrated *in vacuo*. Recrystallization from ethyl acetate—EtOH gave salt **9** (0.55 g, 71%), m.p. 195—196 °C. Found (%): C, 48.51; H, 7.51; I, 39.77; N, 4.01. $C_{13}H_{24}IN$. Calculated (%): C, 48.61; H, 7.53; I, 39.5; N, 4.36. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.35—1.65 (m, 4 H, H(4), H_a(3), H_a(5)); 1.70—1.95 (m, 2 H, H_b(3), H_b(5)); 2.15—2.35 (m, 2 H, H_a(2′), H_a(6′)); 2.55—2.75 (m, 2 H, H_b(2′), H_b(6′)); 3.17 (s, 6 H, Me); 3.60—3.80 (m, 2 H, H(2), H(6)); 4.85—5.1 (m, 4 H, CH_2=); 5.45—5.75 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 15.3 (C(4)), 22.7 (C(3), C(5)), 31.6 (C(2′), C(6′)), 48.9 (Me), 68.5 (C(2), C(6)), 119.1 (CH_2=), 131.5 (—CH=).

***cis*-2,6-Diallyl-1,1-dimethylpiperidinium iodide (10).** By analogy with compound **9**, salt **10** (0.36 g, 67%) was obtained from amine **7** (0.28 g, 1.7 mmol), MeI (0.21 mL, 3.4 mmol), and K_2CO_3 (0.47 g, 3.4 mmol) in 5 mL of EtOH. Iodide **10** is hygroscopic. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.25—1.50 (m, 4 H, H(4), H_a(3), H_a(5)); 1.55—1.75 (m, 2 H, H_b(3), H_b(5)); 1.75—2.00 (m, 2 H, H_a(2′), H_a(6′)); 2.45—2.70 (m, 5 H, H_b(2′), H_b(6′), Me); 3.12 (s, 3 H, Me); 3.55—3.80 (m, 2 H, H(2), H(6)); 4.75—5.05 (m, 4 H, CH_2=); 5.30—5.55 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 20.4 (C(4)), 24.7 (C(3), C(5)),

33.3 (C(2′), C(6′)), 37.7 (Me), 49.0 (Me), 72.0 (C(2), C(6)), 118.7 (CH_2=), 131.0 (—CH=).

The authors are grateful to I. D. Gridnev for recording the $^1H—^1H$ COSY spectra.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 99-03-33125a and 00-03-32807) and by the Council on the RF President Grants and State Support of the Leading Scientific Schools (Project No. 00-15-97378).

References

1. K. Ziegler and H. Zeiser, *Ber.*, 1930, **63**, 1847.
2. E. F. V. Scriven, in *Comprehensive Heterocyclic Chemistry*, Eds. A. R. Katritzky and W. Rees, Pergamon Press, Oxford, 1984, **2**, part **2A**, 262.
3. D. Barr, R. Snaith, R. E. Mulvey, and D. Reed, *Polyhedron*, 1988, **7**, 665.
4. D. R. Armstrong, R. E. Mulvey, D. Barr, R. Snaith, and D. Reed, *J. Organomet. Chem.*, 1988, **313**, 191.
5. W. Clegg, L. Dunbar, L. Horsburgh, and R. E. Mulvey, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 753.
6. Yu. N. Bubnov, E. V. Klimkina, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 467 [*Russ. Chem. Bull.*, 1998, **47**, 451 (Engl. Transl.)].
7. Yu. N. Bubnov, E. A. Shagova, S. V. Evchenko, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 693 [*Russ. Chem. Bull.*, 1994, **43**, 645 (Engl. Transl.)].
8. Y. Kawazoe, M. Tsuda, and M. Ohnbshi, *Chem. Pharm. Bull.*, 1967, **15**, 51, 214.
9. Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1203 [*Russ. Chem. Bull.*, 1995, **44**, 1156 (Engl. Transl.)].
10. Yu. N. Bubnov, *Pure Appl. Chem.,* 1994, **66**, 235.
11. L. I. Zakharkin and V. I. Stanko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1960, 1896 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1960 (Engl. Transl.)].
12. T. V. Talalaeva and K. A. Kocheshkov, in *Metody elementoorganicheskoi khimii* [*Organometallic Methods*], Eds. A. N. Nesmeyanov and K. A. Kocheshkov, Nauka, Moscow, 1971, **1**, 107 (in Russian).
13. W. Robinson and G. M. Sheldrick, *Crystallographic Computing Techniques and New Technologies*, Eds. N. W. Isaacs and M. R. Taylor, Oxford Univ. Press: Oxford, England, 1988, 366.

Received December 25, 2000