Reductive allylation of pyrrole with allylboranes. Synthesis of *trans*- and *cis*-2,5-disubstituted pyrrolidines

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Pyrrole undergoes reductive mono- and diallylation on successive treatment with β,γ-unsaturated organoboron derivatives (triallylborane, allyl(dipropyl)borane, and triprenylborane) and alcohols to give 2-allylated 3-pyrrolines and *trans*-2,5-diallylated pyrrolidines. The addition of both the first and second boron-allylic fragment to the heterocycle proceeds with rearrangement. A method for transformation of the *trans*-2,5-diallylpyrrolidine into the *cis*-isomer (heating with triallylborane at 190 °C) was developed and a series of *N*-substituted derivatives of these pyrrolidines was synthesized. A method for the preparative synthesis of nonsymmetrically substituted *trans*- and *cis*-2-alkyl(phenyl)-5-allylpyrrolidines, based on reductive allylboration of pyrrole followed by 1,2-addition of RLi to the 5-allyl-1-pyrroline that formed, was also developed. A direct confirmation of intermediate formation of 2*H*- and 3*H*-pyrrole tautomers under the action of allylboranes was obtained. The adduct of 2*H*-pyrrole with BF_3 was detected by NMR spectroscopy.

Key words: pyrrole, reductive allylboration, allylboranes, triprenylborane, allylic rearrangement, alkyl(aryl)lithium, 2,5-substituted pyrrolidines, *trans*→*cis*-isomerization, 2-allylated 3-pyrrolines, sigmatropic [1,3]- and [1,5]-hydrogen shifts, adduct of 2*H*-pyrrole with BF_3.

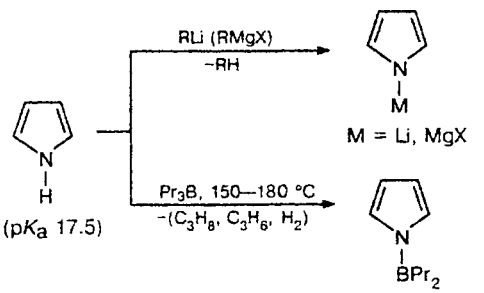
The reaction of reductive mono- or diallylboration of organic nitriles[1] was the first example demonstrated the ability of allylboranes to add to multiple C≡N and C=N bonds. Allylic organoboranes are readily added to the C=N bond of imines,[2–8] quinolines, phenanthridine,[9] and isoquinoline[10] to give (after deboration) the corresponding homoallylic amines or α-allylated dihydro heterocycles. Recently,[11,12] it was established that successive treatment of pyridine and many of its derivatives with corresponding allylboranes and alcohol results in *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridines in 70–97% yields.

All the above-mentioned reactions are inherent *only* in β,γ-unsaturated boron derivatives; they proceed with the allylic rearrangement through a six-membered transition state and are accompanied by the formation of one or two new C–C bonds.

In this work, the results of our study of pyrrole transformations under the action of triallyl- and triprenylborane are reported; the reactions also occur as reductive mono- and *trans*-2,5-diallylation of the heterocycle (for preliminary communications, see Refs. 11, 13, 14).

It is well known that organolithium and organomagnesium compounds readily react with pyrrole to give the corresponding *N*-metallated derivatives[15,16] (Scheme 1).

Scheme 1



Reactions of trialkylboranes with pyrrole proceed only at high temperatures (115–180 °C) to afford *N*-(dialkylboryl)pyrroles.[17,18] A quite different picture is observed in the case of allylboranes.

Reductive allylation of pyrrole

We established that triallylborane and allyl(dipropyl)borane react with pyrrole to give two isomeric addition products **1** and **2**, which differ in position of the double bond in the cycle (Scheme 2).

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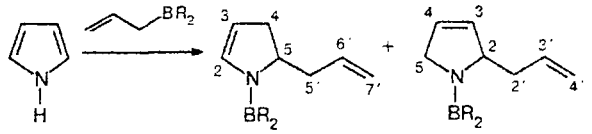
Scheme 2



1a: R = All (65%) **2a:** R = All (35%)
1b: R = Pr (78%) **2b:** R = Pr (22%)

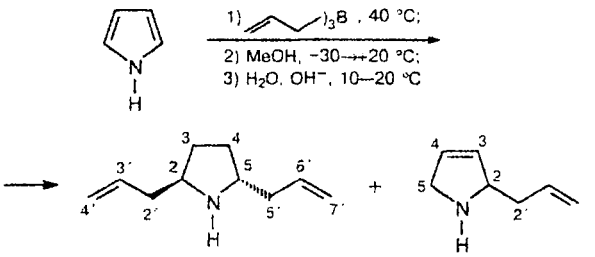
1a + **2a:** δ ^{11}B 42.5
1b + **2b:** δ ^{11}B 45.4

The reaction can be carried out without solvent. In ether, it is completed in 2—3 h at 20 °C or in 30 min at 40—70 °C.

The mixtures of aminoboranes **1a** and **2a** (or **1b** and **2b**) were isolated by vacuum distillation. The **1a** : **2a** and **1b** : **2b** ratios were established from the ^{1}H NMR spectra.

Successive treatment of the products of the reaction between pyrrole and triallylborane (a mixture of compounds **1a** and **2a**) with methanol (3 equiv., from −30 to +20 °C, 1 h) and 10% NaOH (at 20 °C) resulted in a mixture of *trans*-2,5-diallylpyrrolidine **3** and 2-allyl-3-pyrroline **4**, which were isolated by distillation (Scheme 3).

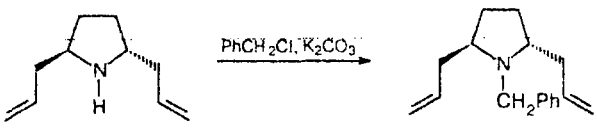
Scheme 3



3 (60%) **4** (16%)

Mutual orientation of allyl groups in amine **3** was established by ^{1}H NMR spectroscopy using a prochiral benzyl probe. To this end, we synthesized the *N*-benzyl derivative **5** by heating amine **3** with benzyl chloride and K_2CO_3 in ethanol (at 80 °C) (Scheme 4).

Scheme 4

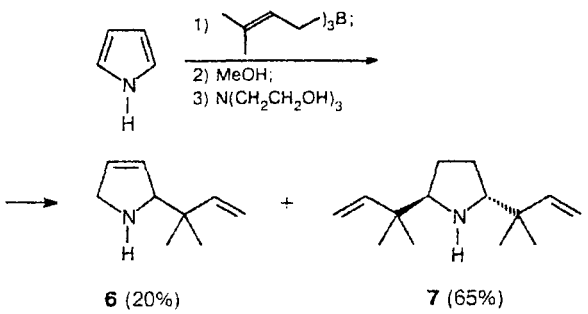


3 **5** (78%)

As in the case of 1-benzyl-*trans*-2,5-dimethylpyrrolidine[19] and 1-benzyl-*trans*-2,6-dipropylpiperidine,[20] the methylene protons (CH_2Ph) appear in the ^{1}H NMR spectrum of compound **5** as an AB-system (dd, 200 MHz, $CDCl_3$, relative to Me_4Si, δ_A 3.67, δ_B 3.91, J_{AB} = 14.0 Hz), which indicates their chemical nonequivalence (diastereotopicity) and, hence, *trans*-orientation of the allyl groups in molecules **5** and **3**.

Successive treatment of pyrrole with triprenylborane, methanol, and triethanolamine resulted in a mixture of 2-(1,1-dimethylallyl)-3-pyrroline (**6**) and *trans*-2,5-bis(1,1-dimethylallyl)pyrrolidine (**7**) (Scheme 5).

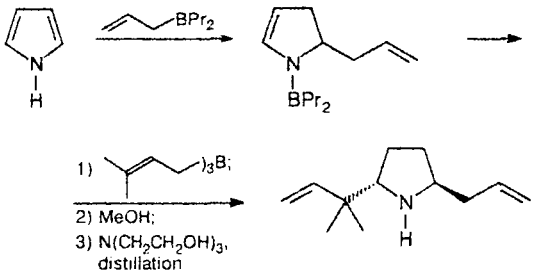
Scheme 5



6 (20%) **7** (65%)

Using two different allylboranes, it is possible to synthesize pyrrolidines with different allylic type groups in positions 2 and 5. Thus, successive treatment of pyrrole with allyl(dipropyl)borane, triprenylborane, methanol, and triethanolamine affords *trans*-2-allyl-5-(1,1-dimethylallyl)pyrrolidine (**8**) (Scheme 6).

Scheme 6



8 (60%)

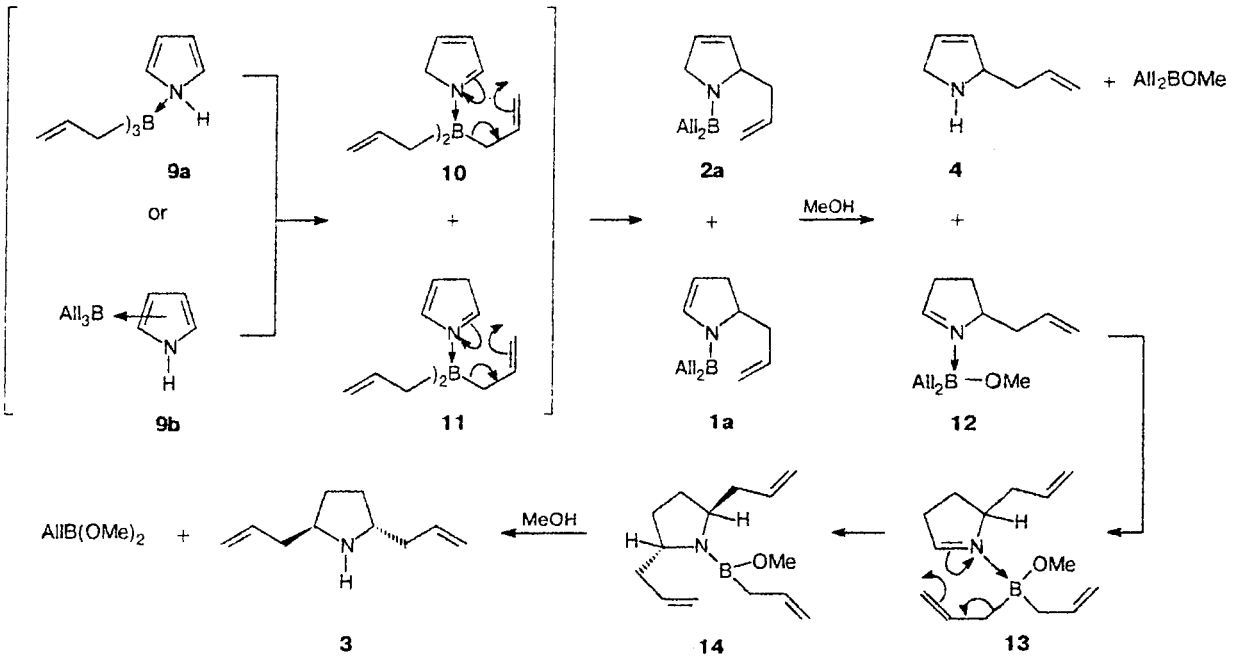
From these results it follows that both steps of the reductive allylboration of pyrrole proceed with allylic rearrangement.

Thus, the reductive *trans*-2,5-diallylation of pyrrole with allylboranes is a general stereoselective reaction, which results in the formation of two new C—C bonds and is accompanied by the "violation of aromaticity" of the heterocycle.

A possible mechanism of mono- and diallylation of pyrrole is shown in Scheme 7.

It can be assumed that the first step of the reaction of pyrrole with triallylborane is the formation of N→B-complex **9a** (or π-complex **9b**). Then, this complex undergoes isomerization by 1,3- and 1,5-migration of the hydrogen atom from the N atom to the C(2) and C(3) atoms to afford two imine adducts **10** and **11**, in which

Scheme 7

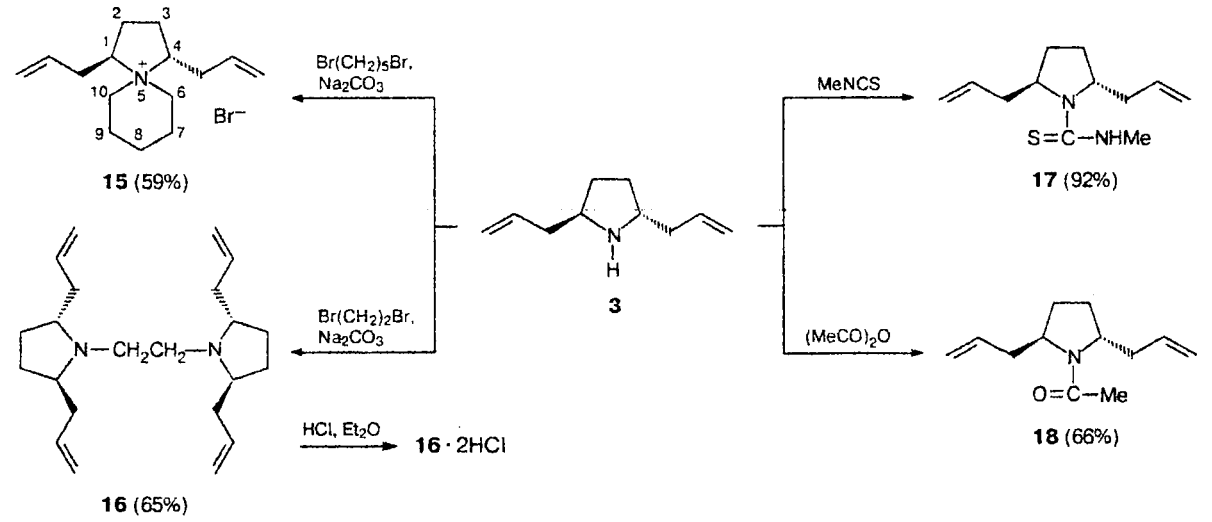


fast allylboration of the C=N bonds occurs (through a six-membered transition state) to give monoallylated aminoborane **2a** and enaminoborane **1a**. These compounds are immediately cleaved with alcohol to give 2-allyl-3-pyrroline **4** (along with All_2BOMe) and a new imine complex **12**. The latter is transformed into aminoborane **14** *via* the six-membered transition state **13**, the addition of the second allylboron fragment proceeding in *trans*-position with respect to the allyl group already present in the ring. Subsequent alcoholysis of aminoborane **14** (cleavage of the B—N bond) results in diallylated reaction product **3** and allyl(dimethoxy)borane.

N-Substituted pyrrolidines

In addition to the benzyl compound **5**, a number of other *N*-substituted *trans*-2,5-diallylpyrrolidines were synthesized. Heating pyrrolidine **3** with 1,5-dibromopentane in *n*-butanol in the presence of Na_2CO_3 resulted in a spiro compound, 1,4-diallyl-5-azoniaspiro[4.5]decane bromide **15**. 1,2-Bis(*trans*-2,5-diallylpyrrolidine-1-yl)ethane (**16**) and its hydrochloride, **16** · 2HCl, were synthesized from amine **3** and 1,2-dibromoethane (Scheme 8).

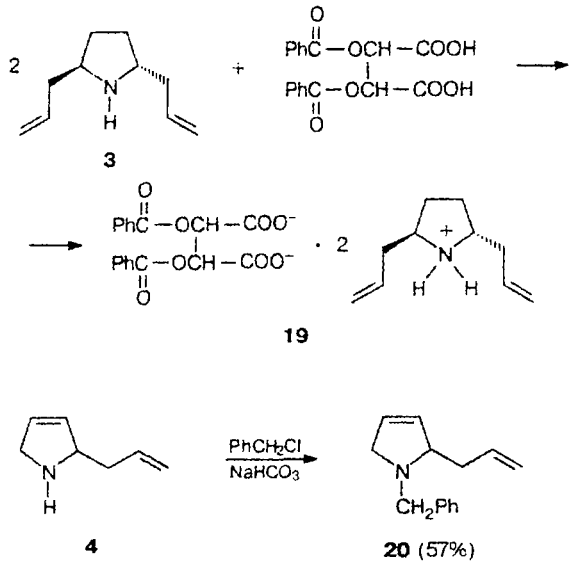
Scheme 8



The reaction of amine **3** with methyl isothiocyanate resulted in thiourea **17**. Treatment of compound **3** with acetic anhydride gave *N*-acetyl derivative **18**.

We made an effort to resolve the racemic amine **3** into the corresponding enantiomers using (+)- and (−)-tartaric, (+)- and (−)-mandelic, and (−)-dibenzoyltartaric ($[\alpha]_D$ −104.02° (EtOH)) acids. However, only in the reaction with (−)-dibenzoyltartaric acid was it possible to isolate a crystalline salt **19** (Scheme 9), whereas oily products were obtained in all other cases. Recrystallization of salt **19** from an AcOEt—MeOH (2 : 1) mixture gave a product with $[\alpha]_D$ −63.25° (MeOH). The *N*-benzyl derivative **20** was synthesized from amine **4** (see Scheme 9).

Scheme 9

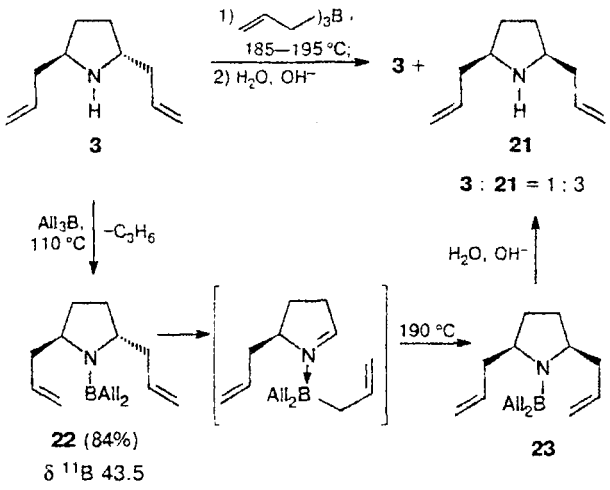


***trans*→*cis*-Isomerization of 2,5-diallylpyrrolidine**

Furthermore, we have found that *trans*-2,5-diallylpyrrolidine (**3**) undergoes isomerization into *cis*-2,5-diallylpyrrolidine (**21**) on heating with triallylborane (Scheme 10).

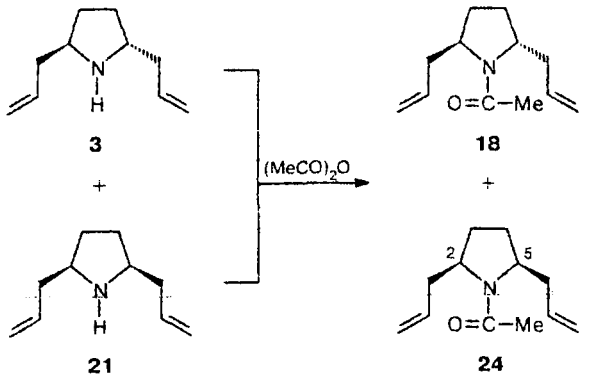
As in the case of *trans*-6-alkyl(aryl)-2-allyl-1,2,3,6-tetrahydropyridines,[21,22] isomerization of *trans*-amine **3** into *cis*-compound **23** occurs most likely by deallylboronation—allylboration (elimination of the allylboron fragment followed by its addition to the C=N bond of the 5-allyl-1-pyrroline that formed). The isomerization was carried out in two steps. Heating amine **3** with triallylborane (at 110 °C) resulted in the cleavage of one B—C bond in the latter, propylene (1 mole) evolution, and the formation of aminoborane **22**, which was isolated by distillation. Further heating aminoborane **22** for 3 h at 185—195 °C (or 10 h at 160 °C) gave a mixture of *trans*- and *cis*-aminoboranes (**22** and **23**, respectively). Isomerization **22** → **23** is not completed even on prolonged heating for 10 h (at 185—195 °C);

Scheme 10



most likely, the ratio **22** : **23** = 1 : 3 (determined from ^{13}C NMR spectra) is the equilibrium ratio. Deboration of a mixture of aminoboranes **23** and **22** with 20% NaOH results in a mixture of *cis*-2,5-diallylpyrrolidine **21** (75%) and *trans*-isomer **3** (25%) (the ratio of the isomers was determined from the ^1H and ^{13}C NMR spectra). Since our attempt to separate these isomers by chromatography failed, we treated a mixture of amines **3** and **21** with acetic anhydride and obtained a mixture of *N*-acetyl derivatives **18** and **24** (in a 1 : 3 ratio), from which *cis*-2,5-diallyl-1-acetylpyrrolidine **24** was isolated by column chromatography on SiO_2 (with ether as eluent) in 64% yield (Scheme 11).

Scheme 11



General procedure for the synthesis of asymmetric 2,5-disubstituted pyrrolidines

It was mentioned above that successive treatment of pyrrole with allyl(dipropyl)borane, triprenylborane, alcohol, and an alkali results in *trans*-2,5-diallylated

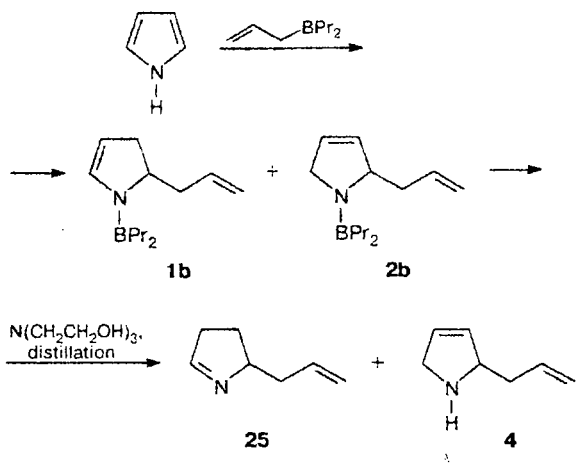
pyrrolidine **8** with *different* substituents in positions 2 and 5. However, both substituents in this compound are of allylic type.

It was desirable to find a general procedure for the synthesis of disubstituted pyrrolidines with different substituents in positions 2 and 5 including alkyl or aryl groups.

Since pyrrole does not add RLi and RMgX, we used a sequence of treatment of this compound with organoboron and organolithium compounds other than that in the asymmetric 2,6-dialkylation of pyridine.[21,23] In the case of pyrrole, allylboration is followed by the reaction with RLi.

Deboration of products of the reaction between pyrrole and allyl(dipropyl)borane (a mixture of compounds **1b** and **2b**, see above) with triethanolamine resulted in a mixture of 5-allyl-1-pyrroline (**25**) and 2-allyl-3-pyrroline (**4**) in a 65 : 35 ratio (Scheme 12), which were distilled off *in vacuo* (the overall yield was 78%).

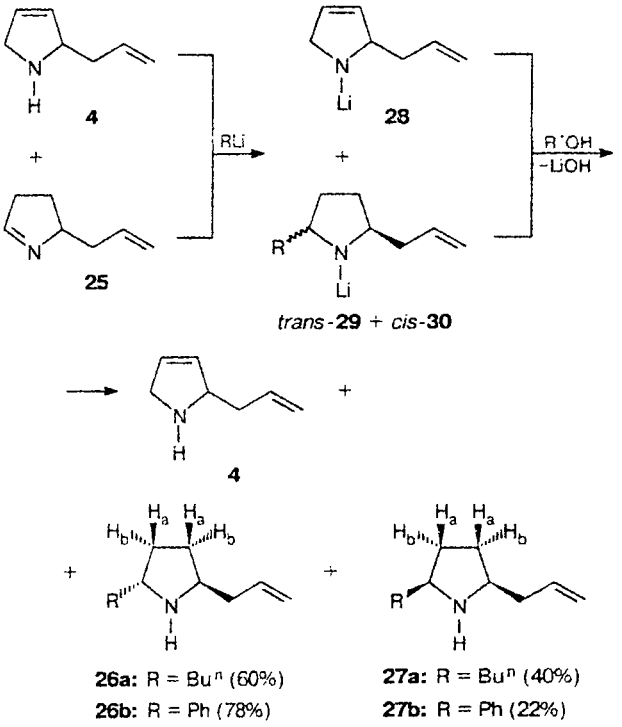
Scheme 12



Successive treatment of the mixture of pyrrolines **4** and **25** with RLi solution (from −60 to −30 °C) and alcohol (at 0 °C) yielded a mixture of *trans*- and *cis*-pyrrolidines (**26** and **27**, respectively) and pyrroline **4** (Scheme 13).

The 1,2-addition reaction of organolithium compound RLi to imine **25** results in a mixture of *trans*- and *cis*-adducts (**29** and **30**, respectively), while the substitution reaction between pyrroline **4** and RLi affords the *N*-lithium compound **28** and hydrocarbon RH. Alcoholysis of lithium amides **28**, **29**, and **30** gave a mixture of amines **4**, **26**, and **27**. Amine **4** was isolated from the mixture of *trans*- and *cis*-pyrrolidines (**26** and **27**, respectively) by vacuum distillation at a reduced pressure (water pump). The **26a** : **27a** and **26b** : **27b** ratios were determined from the ^1H and ^{13}C NMR spectra. The addition can be characterized as a moderately *trans*-stereoselective one. Most likely, the content of *cis*-isomer in the mixture is dependent on the size of radical

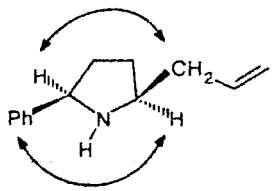
Scheme 13



R in the RLi compound, namely, the more bulky the radical, the lower the content of *cis*-isomer.

The *trans*- and *cis*-isomers **26a,b** and **27a,b** were not isolated as individual compounds. Their structure was confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The mass spectrum (EI) of the **26a** + **27a** mixture contains intense peaks with *m/z* 126 ($[M - C_3H_5]^+$) and 109 ($[M - C_4H_{10}]^+$), while that of the **26b** + **27b** mixture contains intense peaks with *m/z* 186 ($[M - H]^+$), 146 ($[M - C_3H_5]^+$), and 91 ($[C_7H_7]^+$). The assignment of signals in the ^1H NMR spectrum of the **26b** + **27b** mixture was made using ^1H—^1H COSY-45 spectra.

The *trans*-configuration of amine **26b** was determined using two-dimensional (2D) phase-sensitive NOESY spectroscopy.



26b

The cross-peaks observed in the 2D NOESY spectrum between the signals of (1) the H(2) proton and the phenyl group and (2) the H(5) proton and the —CH_2— fragment of the allyl group proves the *trans*-orientation of substituents in the molecule **26b**.

Allylated pyrroline and pyrrolidine derivatives synthesized in this work can be used for the synthesis of natural alkaloids and their analogs, complexones, crown ethers, and other types of heterocycles.

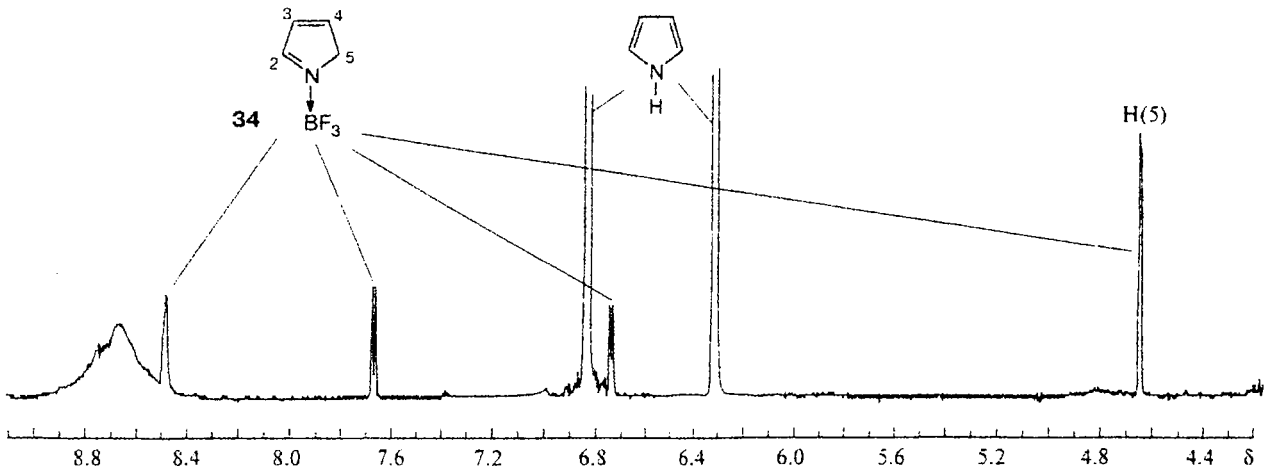
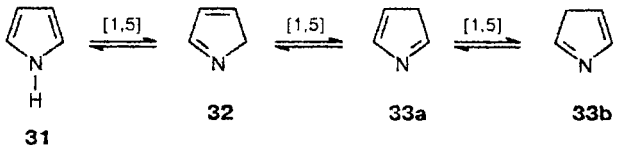


Fig. 1. ^{1}H NMR spectrum of a mixture of pyrrole with $Et_2O \cdot BF_3$ (3 : 2) (400 MHz, $CDCl_3$).

Sigmatropic migrations of H atom in pyrrole ring

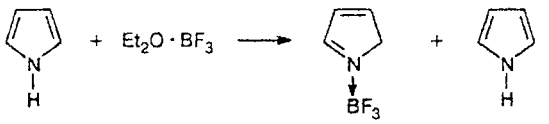
Sigmatropic migrations of hydrogen from the nitrogen atom to C(3) and C(2) atoms in 1*H*-pyrrole (**31**) are likely one of the main factors determining the ability of pyrrole to undergo reductive mono- and *trans*-2,5-diallylation with allylboranes under mild conditions. These migrations result respectively in 2*H*-pyrrole (**32**) and 3*H*-pyrrole (**33a**), which immediately undergo allylboration (see Scheme 7, adducts **10** and **11**). The formation of 2*H*-pyrrole **32** can be explained by sigmatropic [1,5]-hydrogen shift, whereas 3*H*-pyrrole **33** is formed as a result of [1,3]-hydrogen shift or two successive [1,5]-migrations of hydrogen atoms.



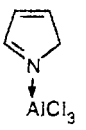
This type of sigmatropic rearrangements has been postulated previously[15,16]; however, all attempts to observe the equilibrium of 1*H*-pyrrole (**31**) with the 2*H*- and 3*H*-tautomers (**32** and **33a**, respectively) failed.

According to recent quantum-chemical calculations,[24] the activation enthalpies of transformations **31** → **32**, **32** → **33a**, and **33a** → **33b** are 44.5, 26.3, and 26.2 kcal mol^{-1}, respectively. It can be assumed that the formation of the 2*H*- and 3*H*-tautomers (**32** and **33a**, respectively) is initiated (or catalyzed) by organoboranes. However, we failed to detect these tautomers or their complexes with triallylborane (**10** and **11**, see Scheme 7) as well as adducts **9a** and **9b** by ^{1}H and ^{11}B NMR spectroscopy.

At the same time, we established by ^{1}H NMR spectroscopy that mixing of pyrrole and boron trifluoride etherate ($BF_3 \cdot OEt_2$) in a 3 : 2 ratio results in the formation of an adduct of 2*H*-pyrrole with $BF_3 \cdot OEt_2$ (**34**) in 10—12% yield (Fig. 1), whereas ~90% of 1*H*-pyrrole **31** forms no complex with BF_3 and remains unchanged (Fig. 1). If $BF_3 \cdot OEt_2$ is taken in excess (1.5 equiv.) the content of adduct **34** in the mixture amounts to 30%.



It should be noted that an adduct **35** of 2*H*-pyrrole was detected previously[25] by NMR spectroscopy for pyrrole treated with a melt of $AlCl_3$ and 1-methyl-3-ethylimidazolium chloride (1.8 : 1.0); to our knowledge, this is the only known analog of complex **34**.



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 and ^{1}H—^{1}H COSY and 2D NOESY NMR spectra were recorded on a Bruker AMX-400 spectrometer (the chemical shifts are reported relative to $SiMe_4$). ^{11}B NMR spectra were recorded on a Bruker AC-200P spectrometer; the chemical shifts are reported relative to $BF_3 \cdot OEt_2$. IR spectra were recorded on an UR-20 spectrophotometer and mass spectra were obtained on Varian MAT and Kratos MS-30 instruments.

Mixture of 5-allyl-1-diallylboryl-2-pyrroline (1a) and 2-allyl-1-diallylboryl-3-pyrroline (2a). Triallylborane (7 g, 9.1 mL, 52 mmol) in 9 mL of dry ether was placed in a three-neck flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an argon inlet. A solution of pyrrole (2.9 g, 3 mL, 43.5 mmol) in 3 mL of ether was added dropwise at 0 °C; the mixture was stirred at the same temperature for 1.5 h and then refluxed for 1 h. Ether and excess triallylborane were distilled

off *in vacuo* to give 7.09 g (81.5%) of a mixture of isomers **1a** and **2a**, b.p. 76.5—78 °C (1 Torr). The **1a** : **2a** ratio (65 : 35) was determined from the ^{1}H NMR spectrum. Found (%): C, 77.47; H, 10.33; B, 4.91; N, 6.61. $C_{13}H_{20}BN$. Calculated (%): C, 77.63; H, 10.02; B, 5.38; N, 6.97. IR (CCl_4), ν/cm^{-1}: 3080, 2975, 2950, 2860, 1710, 1635, 1615, 1445, 1425, 1355, 1235, 1185, 1120, 1000, 918, 900. ^{1}H NMR (200 MHz, $CDCl_3$, the numbering of atoms is shown in Scheme 2), δ: 1.8—2.05 (m, **1a** + **2a**: BCH_2); 2.15—2.48 (m, **1a**: H(5′), $H(4)_a$; **2a**: H(2′)); 2.65—2.85 (m, **1a**: $H(4)_b$); 4.05—4.25 (m, **1a**: H(5); **2a**: CH_2N); 4.5—4.65 (m, **2a**: H(2)); 4.85—5.15 (m, **1a** + **2a**: CH_2=; **1a**: CH=CN); 5.65—6.10 (m, **1a** + **2a**: —CH= in All; **2a**: CH=CH); 6.50—6.59 (m, **1a**: =CHN). ^{13}C NMR ($CDCl_3$), δ: 26.83 (BCH_2); 34.55 (**1a**: C(4)); 41.30 (**1a**: C(5′)); 41.84 (**2a**: C(2′)); 55.13 (**2a**: NCH_2); 57.39 (**1a**: C(5)); 64.90 (**2a**: HCN); 108.05 (**1a**: C(3)); 113.33, 113.51 (**2a**: BCH_2CH=$\underline{C}H_2$); 113.88, 114.13 (**1a**: BCH_2CH=$\underline{C}H_2$); 117.11 (**1a**: C(7′); **2a**: C(4′)); 126.74 (**2a**: C(4)); 130.78 (**2a**: C(3)); 133.81 (**2a**: C(3′)); 133.93 (**1a**: C(2)); 134.16 (**1a**: C(6′)); 136.0, 136.27 (**1a**: $BCH_2\underline{C}H$=); 136.68 (**1a**: $BCH_2\underline{C}H$=). ^{11}B NMR ($CDCl_3$), δ: 42.5 (**1a** + **2a**).

Mixture of 5-allyl-1-dipropylboryl-2-pyrroline (1b) and 2-allyl-1-dipropylboryl-3-pyrroline (2b). Allyl(dipropyl)borane (7.5 g, 54.4 mmol) was placed in a distillation flask, then pyrrole (3.65 g, 54.4 mmol) was added dropwise, and the mixture spontaneously warmed up to 40 °C. Distillation gave 9.27 g (83%) of a mixture of isomers **1b** and **2b**, b.p. 75—76 °C (1 Torr). The **1b** : **2b** ratio was 78 : 22 (determined from the ^{1}H NMR spectrum). IR (neat liquid), ν/cm^{-1}: 3110, 3080, 2960, 2940, 2870, 1645, 1620, 1440, 1410, 1355, 1335, 1310, 1250, 1180, 1125, 990, 960, 915, 700. ^{1}H NMR (200 MHz, C_6D_6), δ: 0.8—1.2 (m, **1b** + **2b**: C_2H_5); 1.3—1.65 (m, **1b** + **2b**: BCH_2); 2.05—2.35 (m, **1b**: H(5′), $H(4)_a$; **2b**: H(2′)); 2.45—2.6 (m, **1b**: $H(4)_b$); 3.85—4.1 (m, **1b**: H(5); **2b**: CH_2N); 4.38—4.52 (m, **2b**: H(2)); 4.75—5.1 (m, **1b**: CH=CN, CH_2=; **2b**: CH_2=); 5.5—5.8 (m, **1b** + **2b**: —CH= in All; **2b**: CH=CH); 6.38—6.52 (m, **1b**: =CHN). ^{13}C NMR (C_6D_6), δ: 18.45, 18.65 (**1b**: CH_3); 18.74, 18.79 (**2b**: CH_3); 19.51, 19.96, 20.00 (**1b** + **2b**: $\underline{C}H_2Me$); 22.31, 23.44 (**1b** + **2b**: BCH_2); 35.40 (**1b**: C(4)); 42.42 (**1b**: C(5′)); 42.96 (**2b**: C(2′)); 56.05 (**2b**: NCH_2); 58.16 (**1b**: C(5)); 65.70 (**2b**: HCN); 107.68 (**1b**: C(3)); 117.61 (**1b**: CH_2=); 117.94 (**2b**: CH_2=); 127.80 (**2b**: C(4)); 131.68 (**2b**: C(3)); 135.06 (**2b**: C(3′)); 135.14 (**1b**: C(6′)); 135.58 (**1b**: HC=N). ^{11}B NMR ($CDCl_3$), δ: 45.4 (**1b** + **2b**).

***trans*-2,5-Diallylpyrrolidine (3) and 2-allyl-3-pyrroline (4).** A solution of triallylborane (27.2 g, 203 mmol) in 27 mL of dry ether was placed in a three-neck flask equipped with a thermometer, a dropping funnel, a reflux condenser, and an argon inlet. A solution of pyrrole (11.33 g, 169 mmol) in 13 mL of dry ether was added dropwise at 0 °C and the reaction mixture was refluxed for 2 h. Then, dry MeOH (25 mL, 618 mmol) was added with caution at −30 °C and the solution was refluxed for 2.5 h. At 0 °C, the reaction mixture was treated with 20% NaOH (45 mL) and stirred for 3 h. Aqueous phase was saturated with NaCl and stirred for 3 h. Organic layer was separated, aqueous layer was extracted with ether (4×20 mL), and the extract was dried over K_2CO_3. The solvents were distilled off at atmospheric pressure and the residue was distilled to give 15.2 g (60%) of amine **3**, b.p. 62—63 °C (6 Torr). Distillation of the fraction with b.p. < 60 °C (6 Torr) on a column with helical metal packing afforded 2.9 g (16%) of amine **4**, b.p. 38—40 °C (12 Torr). ***trans*-2,5-Diallylpyrrolidine (3)**: n_D^{19} 1.4703. Found (%): C, 79.04; H, 11.13; N, 9.48. $C_{10}H_{17}N$. Calculated (%): C, 79.41; H, 11.33; N, 9.26. MS (EI, 70 eV), m/z (I_{rel}): 150 $[M - H]^+$ (11%), 110 $[M - C_3H_5]^+$ (42%), 109 $[M - C_3H_6]^+$ (100%), 97 $[M - CH_2$=$CH-CH$=$CH_2]^+$ (34%), 84 $[M - (C_3H_5 + CN)]^+$ (41%), 82 $[M - (C_3H_6 + HCN)]^+$ (39%), 71 $[M - (CH_2$=$CH-CH$=$CH_2 + C_2H_2)]^+$ (42%), 69 $[M - 2C_3H_5]^+$ (61%), 68 $[M - (C_3H_5 + C_3H_6)]^+$ (71%), 67 $[M - 2C_3H_6]^+$ (78%), 56 $[M - (CH_2$=$CH-CH$=$CH_2 + C_3H_5)]^+$ (34%), 55 $[M - (CH_2$=$CH-CH$=$CH_2 + C_3H_6)]^+$ (66%). IR (neat liquid), ν/cm^{-1}: 3300 (br), 3080, 2960, 2920, 2870, 1835, 1645, 1415, 1350, 1300, 1220, 1115, 910. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.20—1.45 (m, 2 H, $H(3)_a$, $H(4)_a$); 1.50—1.72 (br.s, 1 H, NH); 1.72—2.00 (m, 2 H, $H(3)_b$, $H(4)_b$); 2.00—2.24 (m, 4 H, —CH_2— in All); 3.05—3.28 (m, 2 H, HCN); 4.85—5.10 (m, 4 H, CH_2=); 5.60—5.88 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 31.27 (C(3), C(4)); 41.12 (—CH_2— in All); 56.78 (CN); 116.24 (CH_2=); 136.22 (—CH=). **2-Allyl-3-pyrroline (4)**: n_D^{19} 1.4770. Found (%): C, 77.25; H, 10.15; N, 12.69. $C_7H_{11}N$. Calculated (%): C, 77.01; H, 10.16; N, 12.83. MS (EI, 70 eV), m/z (I_{rel}): 109 $[M]^+$ (29%), 107 $[M - 2H]^+$ (40%), 79 $[M - NH_2CH_2]^+$ (44%), 69 $[M - C_3H_4]^+$ (27%), 68 $[M - C_3H_5]^+$ (100%), 67 $[M - C_3H_6]^+$ (65%), 53 $[M - (NH_2CH_2 + C_2H_2)]^+$ (33%). IR (neat liquid), ν/cm^{-1}: 3240 (br), 3080, 2900, 2850, 1835, 1642, 1445, 1415, 1345, 1115, 1090, 1000, 915, 800, 710. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.80 (s, 1 H, NH); 2.10—2.35 (m, 2 H, —CH_2— in All); 3.6—3.85 (m, 2 H, CH_2N); 3.95—4.10 (m, 1 H, HCN); 4.95—5.15 (m, 2 H, CH_2=); 5.65—5.95 (m, 3 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 41.10 (—CH_2— in All); 53.58 (CH_2N); 64.57 (HCN); 116.82 (CH_2=); 128.66 (C(4)); 131.81 (C(3)); 135.37 (C(3′)).

***trans*-2,5-Diallylpyrrolidine hydrochloride (3 · HCl)** was obtained from amine **3** (0.85 g) and a solution of HCl in ether. The yield was 0.89 g (89%), m.p. 138—139 °C. Found (%): C, 64.36; H, 9.91; N, 7.66, Cl, 18.84. $C_{10}H_{17}N \cdot HCl$. Calculated (%): C, 63.99; H, 9.66; N, 7.46. Cl, 18.89. IR (CH_2Cl_2), ν/cm^{-1}: 3420 (br), 2900, 2755, 2695, 2545, 2485, 2180, 1860, 1645, 1590, 1435, 1415, 1290, 1035, 995, 925. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.60—1.85 (m, 2 H, $H(3)_a$, $H(4)_a$); 2.00—2.30 (m, 2 H, $H(3)_b$, $H(4)_b$); 2.40—2.65 (m, 2 H, $H(2')_a$, $H(5')_a$); 2.70—2.95 (m, 2 H, $H(2')_b$, $H(5')_b$); 3.60—3.85 (m, 2 H, HCN); 5.05—5.35 (m, 4 H, CH_2=); 5.65—5.95 (m, 2 H, —CH=); 9.65 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 29.61 (C(3), C(4)); 36.61 (—CH_2— in All); 56.74 (CN); 119.16 (CH_2=); 132.32 (—CH=).

2-Allyl-3-pyrroline hydrochloride (4 · HCl) was obtained from amine **4** (0.64 g, 5.4 mmol) and a solution of HCl in ether. The yield was 92%, m.p. 89—90 °C. IR ($CHCl_3$), ν/cm^{-1}: 3420 (br), 2980, 2910, 2800, 2695, 2600, 2460, 1735, 1645, 1580, 1430, 1375, 1245, 1125, 1040, 990, 930. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 2.5—2.9 (m, 2 H, —CH_2— in All); 4.0—4.3 (m, 2 H, CH_2N); 4.5—4.7 (m, 1 H, HCN); 5.2—5.5 (m, 2 H, CH_2=); 5.75—6.05 (m, 3 H, —CH=); 10.13 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 35.72 (—CH_2— in All); 50.60 (CH_2N); 64.28 (HCN); 116.79 (CH_2=); 124.06 (C(4)); 127.67 (C(3)); 130.63 (C(3′)).

***trans*-2,5-Diallyl-1-benzylpyrrolidine (5).** A mixture of amine **3** (1.89 g, 12.5 mmol), $PhCH_2Cl$ (1.44 mL, 12.5 mmol), $NaHCO_3$ (1.3 g), and EtOH (5 mL) was refluxed for 3 h. The residue was filtered off and the filtrate was distilled *in vacuo* to remove EtOH. Water (10 mL) and 4 mL of 20% NaOH was added to the residue and the mixture was extracted with ether (3×10 mL). The ethereal fractions were washed with saturated NaCl solution and dried (K_2CO_3). Distillation gave 2.35 g (78%) of compound **5**, b.p. 115—116 °C (1 Torr), n_D^{19} 1.5248. MS (EI, 70 eV), m/z (I_{rel}): 241 $[M]^+$ (2%), 201 $[M - C_3H_4]^+$ (39%), 200 $[M - C_3H_5]^+$ (100%), 158 $[M - (C_3H_6 + C_3H_5)]^+$ (4%), 92 $[C_7H_8]^+$ (33%), 91 $[C_7H_7]^+$ (99%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.4—1.7 (m, 2 H,

H(3)$_a$, H(4)$_a$); 1.7—2.1 (m, 4 H, —CH$_2$— in All); 2.15—2.45 (m, 2 H, H(3)$_b$, H(4)$_b$); 2.85—3.05 (m, 2 H, HCN); 3.55—3.75 (d, 1 H, N—CH—Ph, J_{AB} = 14.0 Hz); 3.8—4.00 (d, 1 H, N—CH—Ph, J_{AB} = 14.0 Hz); 4.85—5.15 (m, 4 H, CH$_2$=); 5.5—5.85 (m, 2 H, —CH= in All); 7.1—7.5 (m, 5 H, Ph). ^{13}C NMR (CDCl$_3$), δ: 27.45 (C(3), C(4)); 35.32 (—CH$_2$— in All); 51.30 (NCH$_2$); 59.67 (NCH); 116.02 (CH$_2$=); 126.45 (C_p); 128.03, 128.14 (C_o, C_m); 136.37 (—CH= in All); 140.39 (C_i).

***trans*-2,5-Diallyl-1-benzylpyrrolidine hydrochloride (5 · HCl)** was obtained from amine **5** (0.77 g) and a solution of HCl in ether. The yield was 0.79 g (89%); the hydrochloride is hygroscopic. IR (CH$_2$Cl$_2$), ν/cm^{-1}: 3420 (br), 3050, 2975, 2400, 2320, 1650, 1460, 1400, 1290, 995, 930. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 1.65—2.7 (m, 7 H, H(3), H(4), H(2′), H(5′)$_a$); 2.7—2.95 (m, 1 H, H(5′)$_b$); 3.25—3.55 (m, 1 H, HCN); 3.8—4.1 (m, 2 H, NCH, N—CH—Ph); 4.2—4.45 (m, 1 H, N—CH—Ph); 4.8—5.3 (m, 4 H, CH$_2$=); 5.35—5.8 (m, 2 H, —CH= in All); 7.35—7.6 (m, 3 H, Ph); 7.75—8.0 (m, 2 H, Ph); 12.2 (br.s, 1 H, NH). ^{13}C NMR (CDCl$_3$), δ: 26.52, 27.95 (C(3), C(4)); 32.37, 36.57 (—CH$_2$— in All); 53.20 (NCH$_2$); 64.20, 65.44 (NCH); 119.04, 119.42 (CH$_2$=); 129.15, 129.56, 130.67 (Ph); 131.94, 132.06 (—CH= in All).

2-(1,1-Dimethylallyl)-3-pyrroline (6) and *trans*-2,5-bis(1,1-dimethylallyl)pyrrolidine (7). Triprenylborane (5.7 g, 26.1 mmol) was placed in a three-neck flask equipped with a thermometer, a dropping funnel, a reflux condenser, and an argon inlet and pyrrole (1.64 g, 24.4 mmol) was added dropwise. The reaction mixture was stirred for 1 h at room temperature and for an additional 0.5 h at 60 °C. Then, a solution of dry MeOH (1.05 mL, 26.1 mmol) in 1 mL of dry ether was added with caution at −40 °C and the mixture was refluxed for 1 h. Ether was distilled off at a reduced pressure (water pump). Triethanolamine (5.2 mL, 5.84 g, 39.2 mmol) was added to the residue and products boiling in the temperature range 30—100 °C were distilled off (2 Torr). Repeated distillation gave 0.67 g (20%) of amine **6**, b.p. 68—70 °C (15 Torr), and 3.29 g (65%) of amine **7**, b.p. 117—118 °C (15 Torr). **2-(1,1-Dimethylallyl)-3-pyrroline (6)**: n_D^{19} 1.4751. IR (neat liquid), ν/cm^{-1}: 3370 (br), 3080, 1641, 910. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 0.95 (s, 3 H, Me); 0.96 (s, 3 H, Me); 1.87 (br.s, 1 H, NH); 3.65—3.75 (m, 2 H, CH$_2$N); 3.75—3.85 (m, 1 H, HCN); 4.90—5.05 (m, 2 H, CH$_2$=); 5.70—5.95 (m, 3 H, —CH=). ^{13}C NMR (CDCl$_3$), δ: 23.03 (Me); 23.17 (Me); 41.23 (CMe); 54.10 (CH$_2$N); 74.08 (HCN); 111.86 (CH$_2$=); 129.07 (C(4)); 129.5 (C(3)); 145.89 (C(3′)). ***trans*-2,5-Bis(1,1-dimethylallyl)pyrrolidine (7)**: n_D^{19} 1.4724. IR (neat substance), ν/cm^{-1}: 3370 (br); 3085, 1641, 910. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 0.94 (s, 6 H, Me); 0.97 (s, 6 H, Me); 1.20—1.55 (m, 3 H, H(3)$_a$, H(4)$_a$, NH); 1.60—1.80 (m, 2 H, H(3)$_b$, H(4)$_b$); 2.85—3.00 (m, 2 H, HCN); 4.90—5.00 (m, 4 H, CH$_2$=); 5.75—5.95 (m, 2 H, —CH=). ^{13}C NMR (CDCl$_3$), δ: 23.01 (Me); 24.53 (Me); 27.63 (C(3), C(4)); 40.26 (CMe); 67.04 (CN); 111.72 (CH$_2$=); 146.05 (—CH=).

***trans*-2,5-Bis(1,1-dimethylallyl)pyrrolidine hydrochloride (7 · HCl)** was obtained from amine **7** and a solution of HCl in ether, m.p. 252—254 °C (with decomp.). ^{1}H NMR (200 MHz, CDCl$_3$), δ: 1.26 (s, 6 H, Me); 1.34 (s, 6 H, Me); 1.65—2.1 (m, 4 H, H(3), H(4)); 3.55—3.75 (m, 2 H, HCN); 5.05—5.3 (m, 4 H, CH$_2$=); 6.0—6.25 (m, 2 H, —CH=); 8.85 (br.s, 2 H, NH). ^{13}C NMR (CDCl$_3$), δ: 24.15 (Me); 24.37 (Me); 25.99 (C(3), C(4)); 38.5 (CMe); 69.15 (CN); 114.73 (CH$_2$=); 142.16 (—CH=).

***trans*-2-Allyl-5-(1,1-dimethylallyl)pyrrolidine (8).** To a mixture of 5.91 g (28.8 mmol) of aminoboranes **1b** and **2b** (the **1b** : **2b** ratio was 78 : 22, see above) in 15 mL of dry ether, triprenylborane (6.28 g, 28.8 mmol) was added. A solution of dry MeOH (2.32 mL, 57.6 mmol) in 2.5 mL of dry ether was added with caution at −40 °C. The reaction mixture was slowly heated to 20 °C and refluxed for 1 h. The solvents were distilled off at a reduced pressure (water pump), triethanolamine (11.4 mL, 12.8 g, 85.9 mmol) was added to the residue, and the product was distilled off on an oil bath at a reduced pressure (oil pump) to give 3.34 g (60%) of amine **8**, b.p. 62—64 °C (1 Torr), n_D^{19} 1.4721. IR (neat liquid), ν/cm^{-1}: 3360 (br), 3082, 1643, 912. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 0.94 (s, 3 H, Me); 0.97 (s, 3 H, Me); 1.25—1.95 (m, 5 H, H(3), H(4), NH); 2.0—2.3 (m, 2 H, —CH$_2$— in All); 2.95—3.20 (m, 2 H, HCN); 4.90—5.15 (m, 4 H, CH$_2$=); 5.65—5.95 (m, 2 H, —CH=). ^{13}C NMR (CDCl$_3$), δ: 22.94 (Me); 24.41 (Me); 26.80, 32.09 (C(3), C(4)); 40.15 (CMe); 40.85 (—CH$_2$— in All); 57.91, 65.94 (CN); 111.8 (CH$_2$=CHCMe$_2$); 116.29 (CH$_2$= in All); 136.14 (—CH= in All); 145.84 (—CH= in 1,1-dimethylallyl).

***trans*-2-Allyl-5-(1,1-dimethylallyl)pyrrolidine hydrochloride (8 · HCl)** was obtained from amine **8** and a solution of HCl in ether, m.p. 143.5—145.5 °C. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 1.23 (s, 3 H, Me); 1.33 (s, 3 H, Me); 1.55—1.9 (m, 2 H, H(3)$_a$, H(4)$_a$); 1.9—2.3 (m, 2 H, H(3), H(4)$_b$); 2.45—2.75 (m, 1 H, H(2′)$_a$); 3.05—3.3 (m, 1 H, H(2′)$_b$); 3.35—3.9 (m, 2 H, HCN); 5.0—5.35 (m, 4 H, CH$_2$=); 5.6—5.9 (m, 1 H, —CH= in All); 5.9—6.15 (m, 1 H, CH$_2$=CHCMe$_2$); 8.9 (br.s, 1 H, NH); 9.85 (br.s, 1 H, NH). ^{13}C NMR (CDCl$_3$), δ: 23.72 (Me); 25.77, 29.52 (C(3), C(4)); 35.64 (CMe); 38.51 (—CH$_2$— in All); 60.47, 67.1 (CN); 115.41, 118.13 (CH$_2$=); 132.36 (—CH= in All); 140.88 (=CH—CMe).

***trans*-1,4-Diallyl-5-azoniaspiro[4.5]decane bromide (15).** Amine **3** (1.3 g, 8.6 mmol), 1,5-dibromopentane (1.98 g, 1.16 mL, 8.6 mmol), Na$_2$CO$_3$ (1 g), and Bu^{n}OH (10 mL) were placed in a single-neck flask equipped with a reflux condenser and an argon inlet. The reaction mixture was refluxed for 50 h; the residue was filtered off and washed with acetone. The solvents were removed *in vacuo* and the residue (a salt) was washed with ether. Recrystallization of the residue from an ether—CH$_2$Cl$_2$ (2 : 1) mixture followed by freezing for 12 days gave 1.51 g (59%) of compound **15** as white needle-shaped crystals, m.p. 212—214 °C. Found (%): C, 59.60; H, 8.69; N, 4.58; Br, 26.51. C$_{15}$H$_{26}$BrN. Calculated (%): C, 60.0; H, 8.73; N, 4.66, Br, 26.61. MS (CI), *m/z* (I_{rel}): 302 [M + 2H]$^+$ (13%), 301 [MH]$^+$ (6%), 300 [M]$^+$ (18%), 260 [MH − C$_3$H$_5$]$^+$ (34%), 258 [M − C$_3$H$_6$]$^+$ (28%), 221 [MH$_2$ − HBr]$^+$ (22%), 220 [MH − HBr]$^+$ (100%), 218 [M − 2 C$_3$H$_5$]$^+$ (24%), 178 [M − (C$_3$H$_5$ + HBr)]$^+$ (55%), 138 [MH − (2 C$_3$H$_5$ + HBr)]$^+$ (37%). IR (KBr pellets), ν/cm^{-1}: 3440 (br), 3070, 2980, 2940, 2870, 1640, 1470, 1445, 1415, 1325, 1060, 1015, 1005, 950, 915, 890, 850. ^{1}H NMR (200 MHz, CDCl$_3$), δ: 1.6—2.10 (m, 8 H, C—CH$_2$—C); 2.1—2.55 (m, 4 H, C—CH$_2$—C); 2.55—2.81 (m, 2 H, C—CH$_2$—C); 3.35—3.55 (m, 4 H, CH$_2$N); 3.95—4.15 (m, 2 H, HCN); 4.95—5.25 (m, 4 H, CH$_2$=); 5.55—5.85 (m, 2 H, —CH=). ^{13}C NMR (CDCl$_3$), δ: 20.94 (C(7), C(8), C(9)); 24.38 (C(2), C(3)); 32.90 (—CH$_2$— in All); 53.84 (NCH$_2$); 69.35 (HCN); 119.77 (CH$_2$=); 131.57 (—CH=).

1,2-Bis(*trans*-2,5-diallylpyrrolidine-1-yl)ethane (16). 1,2-Dibromoethane (3.15 g, 1.45 mL, 16.8 mmol), Na$_2$CO$_3$ (6.5 g), amine **3** (5.08 g, 33.6 mmol), and dry Bu^{n}OH (16 mL) were placed in a single-neck flask equipped with a reflux condenser and an argon inlet. The reaction mixture was refluxed for 40 h (the reaction was monitored by TLC). The solvent and the unreacted 1,2-dibromoethane and amine **3** were distilled off *in vacuo*. Then water (20 mL) was added and amine **16** was extracted with ether (3×10 mL). The ethereal fractions were washed with saturated NaCl solution and dried (K$_2$CO$_3$). Distil-

lation gave 3.6 g (65%) of compound **16** as an oil, b.p. 130—135 °C (1 Torr), n_D^{19} 1.4980. Found (%): C, 80.81; H, 10.93; N, 8.30. $C_{22}H_{36}N_2$. Calculated (%): C, 80.43; H, 11.04; N, 8.53. MS (CI), *m/z* (I_{rel}): 329 $[MH]^+$ (28%), 328 $[M]^+$ (5%), 327 $[M - H]^+$ (20%), 288 $[MH - C_3H_5]^+$ (35%), 287 $[M - C_3H_5]^+$ (100%), 178 $[M - C_{10}H_{16}N]^+$ (32%), 164 $[M/2]^+$ (95%). IR (neat liquid), ν/cm^{-1}: 3080, 2970, 2920, 2845, 2820, 2710, 1830, 1640, 1470, 1440, 1420, 1355, 1300, 1220, 1165, 1120, 995, 915. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.45—1.7 (m, 4 H, $H(3)_a$, $H(4)_a$); 1.7—2.05 (m, 8 H, $-CH_2-$ in All); 2.3—2.5 (m, 4 H, $H(3)_b$, $H(4)_b$); 2.55—3.05 (m, 8 H, HCN, CH_2N); 4.95—5.15 (m, 8 H, $CH_2=$); 5.6—5.9 (m, 4 H, $-CH=$). ^{13}C NMR ($CDCl_3$), δ: 27.51 (C(3), C(4)); 35.18 ($-CH_2-$ in All); 46.26, 46.44 (HCN); 60.25, 60.47 (CH_2N); 116.20 ($CH_2=$); 136.30 ($-CH=$).

1,2-Bis(*trans*-2,5-diallylpyrrolidine-1-yl)ethane hydrochloride (16·2HCl) was obtained from amine **16** (0.57 g, 1.73 mmol) and a solution of HCl in ether, yield 90%, a mixture of two diastereomers with m.p. 201—203 °C and 248—250 °C; the latter was isolated by crystallization from an ether—methanol mixture. ^1H NMR (200 MHz, D_2O), δ: 1.85—2.75 (m, 16 H, H(3), H(4), $-CH_2-$ in All); 3.45—3.75 (m, 14 H, HCN); 3.8—4.1 (m, 4 H, CH_2N); 5.15—5.45 (m, 8 H, $CH_2=$); 5.65—5.95 (m, 4 H, $-CH=$); 12.45 (br.s, 2 H, NH). ^{13}C NMR (D_2O), δ: 26.37 (C(3), C(4)); 33.35 ($-CH_2-$ in All); 42.53, 42.72 (HCN); 65.23 (CH_2N); 120.0 ($CH_2=$); 131.68 ($-CH=$).

***trans*-2,5-Diallyl-1-methylaminothiocarbonylpyrrolidine (17).** A solution of methyl isothiocyanate (0.42 g, 5.8 mmol) in dry ether (3 mL) was added to a solution of amine **3** (0.89 g, 5.8 mmol) in dry ether (7 mL). The solution was refluxed for 5 h and ether was removed *in vacuo*. The white residue that formed was washed with dry pentane to give compound **17** (1.13 g, 92%), m.p. 75—76 °C. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.65—2.15 (m, 6 H, H(3), H(4), H(2′)); 2.4—3.0 (br.m, 2 H, H(5′)); 3.1 (d, 3 H, Me, J = 4.27 Hz); 3.75—4.7 (br.m, 2 H, HCN); 4.9—5.2 (m, 4 H, $CH_2=$); 5.45—5.85 (m, 3 H, $-CH=$, NH). ^{13}C NMR ($CDCl_3$), δ: 25.84 (C(3), C(4)); 32.07 (Me); 36.27 ($-CH_2-$ in All); 58.26, 61.56 (HCN); 117.35 ($CH_2=$); 134.69 ($-CH=$); 179.00 (C=S).

***trans*-2,5-Diallyl-1-acetylpyrrolidine (18).** Amine **3** (0.87 g, 5.75 mmol) was placed in a three-neck flask equipped with a thermometer, a reflux condenser, and a dropping funnel. Acetic anhydride (0.82 mL, 0.89 g, 8.72 mmol) was added with caution at 0 °C and the mixture spontaneously warmed up to 80 °C. Then, the mixture was heated for 10 min on a boiling water bath, H_2O (2 mL) and saturated $NaHCO_3$ solution (10 mL) were added at 20 °C, and the acetate **18** that formed was extracted with ether. The extract was dried (K_2CO_3). Distillation gave 0.73 g (66%) of compound **18**, b.p. 90—92 °C (1 Torr), n_D^{19} 1.4917. Found (%): C, 74.81; H, 9.83; N, 7.39. $C_{12}H_{19}NO$. Calculated (%): C, 74.57; H, 9.91; N, 7.25. MS (EI, 70 eV), *m/z* (I_{rel}): 193 $[M]^+$ (4%), 192 $[M - H]^+$ (5%), 152 $[M - C_3H_5]^+$ (34%), 151 $[M - CH_2=C=O]^+$ (70%), 110 $[M - (C_3H_5 + CH_2=C=O)]^+$ (46%), 109 $[M - (C_3H_5 + MeCO)]^+$ (100%), 93 $[M - (C_3H_5 + MeCONH_2)]^+$ (35%), 81 $[M - (C_3H_5 + MeCO + CHNH)]^+$ (22%), 69 $[M - (2\,C_3H_5 + CH_2=C=O)]^+$ (36%), 68 $[M - (2\,C_3H_5 + MeCO)]^+$ (52%), 67 $[M - (C_3H_5 + C_3H_6 + MeCO)]^+$ (53%). IR (neat substance), ν/cm^{-1}: 3460 (br), 3260 (br), 3080, 2970, 2940, 2880, 1830, 1640, 1405, 1355, 1240, 1185, 1170, 1060, 1035, 1000, 920, 855, 730, 645, 610, 550. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.65—2.22 (m, 9 H, H(3), H(4), Me, NH, H(5′)); 2.25—2.4 (m, 1 H, $H(2')_b$); 2.6—2.8 (m, 1 H, $H(2')_a$); 3.75—3.9 (m, 1 H, H(5)); 4.05—4.2 (m, 1 H, H(2)); 5.0—5.15 (m, 4 H, $CH_2=$); 5.6—5.9 (m, 2 H, $-CH=$). ^{13}C NMR ($CDCl_3$), δ: 22.84 (Me); 25.49 (C(4)); 27.27 (C(3)); 36.30 (C(5′)); 39.25 (C(2′)); 56.73 (C(5)); 58.51 (C(2)); 116.80, 117.70 ($CH_2=$); 134.02, 135.25 ($-CH=$); 168.74 (C=O).

Bis(*trans*-2,5-diallylpyrrolidine-1-ium)dibenzoyltartrate(2−) (19). (−)-Dibenzoyltartaric acid ($[\alpha]_D$ −104.02° (*c* 1.03, EtOH), 3.79 g, 10.1 mmol) and dry $CHCl_3$ (7 mL) were placed in a single-neck flask equipped with a reflux condenser and an argon inlet. Then, *trans*-2,5-diallylpyrrolidine **3** (3.1 g, 20.5 mmol) was added at 0 °C. To the refluxing solution, dry $CHCl_3$ (13 mL) was added until complete dissolution of the residue that formed. The solvent was evaporated *in vacuo* and recrystallization from an ethyl acetate—methanol (2 : 1) mixture gave 5.57 g (84%) of salt **19**, m.p. 146—152 °C, $[\alpha]_D$ −63.25° (*c* 1, MeOH). ^1H NMR (200 MHz, $CDCl_3$), δ: 1.0—1.45 (m, 4 H, $H(3)_a$, $H(4)_a$); 1.5—1.85 (m, 4 H, $H(3)_b$, $H(4)_b$); 1.85—2.15 (m, 4 H, $H(2')_a$, $H(5')_a$); 2.15—2.5 (m, 4 H, $H(2')_b$, $H(5')_b$); 3.05—3.45 (m, 4 H, H(2), H(5)); 4.6—5.0 (m, 8 H, $CH_2=$); 5.15—5.5 (m, 4 H, $-CH=$); 5.83 (s, 2 H, OCH); 7.15—7.55 (m, 6 H, Ph); 7.9—8.2 (m, 4 H, Ph); 9.84 (br.s, 4 H, NH). ^{13}C NMR ($CDCl_3$), δ: 29.25, 29.46 (C(3), C(4)); 36.17 ($-CH_2-$ in All); 57.73 (HCN); 75.56 (OCH); 117.69 ($CH_2=$); 128.07, 129.78 (C_o, C_m); 130.89 (C_i); 132.42 (C_p); 133.02, 133.17 ($-CH=$); 165.80, 171.75 (C=O).

2-Allyl-1-benzyl-3-pyrroline (20) was obtained analogously to the synthesis of compound **5** from amine **4** (0.79 g, 7.2 mmol), $PhCH_2Cl$ (0.91 g, 0.82 mL, 7.2 mmol), EtOH (5 mL), and $NaHCO_3$ (0.65 g). The yield of compound **20** was 0.82 g (57%), b.p. 94—95 °C (1 Torr), n_D^{19} 1.5324. Found (%): C, 84.60; H, 8.53; N, 6.91. $C_{14}H_{17}N$. Calculated (%): C, 84.37; H, 8.60; N, 7.03. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 199 $[M]^+$ (4%), 197 $[M - 2H]^+$ (18%), 158 $[M - C_3H_5]^+$ (79%), 91 $[C_7H_7]^+$ (100%). IR (neat liquid), ν/cm^{-1}: 3430 (br), 3065, 3015, 2970, 2920, 2870, 2790, 1640, 1605, 1490, 1455, 1435, 1375, 1360, 1330, 1290, 1250, 1210, 1135, 1075, 1030, 1015, 1000, 915, 875, 830, 750, 700, 680, 470. ^1H NMR (200 MHz, $CDCl_3$), δ: 2.15—2.45 (m, 2 H, $-CH_2-$ in All); 3.10—3.35 (m, 1 H, NCH); 3.45—3.80 (m, 3 H, $N-CH_a-Ph$, H(5)); 4.00—4.20 (m, 1 H, $N-CH_b-Ph$); 4.95—5.20 (m, 2 H, $CH_2=$); 5.65—6.00 (m, 3 H, $-CH=$); 7.15—7.50 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 39.72 ($-CH_2-$ in All); 58.73 (C(5)); 60.24 ($N-CH_2Ph$); 69.98 (C(2)); 116.27 ($CH_2=$); 126.67, 127.00 (C_p, C(4)); 128.11, 128.42 (C_o, C_m); 130.88 (C(3)); 135.70 (C(3′)); 140.01 (C_i).

***trans*-2,5-Diallyl-1-(diallylboryl)pyrrolidine (22).** Amine **3** (1.37 g, 9 mmol) was placed in a two-neck flask equipped with a reflux condenser, a dropping funnel, and an argon inlet. Triallylborane (1.31 g, 1.7 mL, 10 mmol) was added at 10 °C and the reaction mixture was heated at 110 °C for 1 h until propylene evolution ceased. Distillation gave 1.84 g (84%) of aminoborane **22**, b.p. 89—90 °C (1 Torr). Found (%): C, 78.70; H, 10.61; B, 4.60. $C_{16}H_{26}BN$. Calculated (%): C, 79.02; H, 10.78; B, 4.44. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.65—2.3 (m, 12 H, $-CH_2-$); 3.8—3.9 (m, 2 H, HCN); 4.85—5.1 (m, 8 H, $CH_2=$); 5.6—6.1 (m, 4 H, $-CH=$). ^{13}C NMR ($CDCl_3$), δ: 27.24 (C(3), C(4)); 27.89 ($B-CH_2-$); 43.24 ($-CH_2-$ in All); 58.86 (HCN); 113.73 ($B-CH_2CH=CH_2$); 116.68 (C(4′), C(7′)); 135.91 (C(3′), C(6′)); 137.02 ($B-CH_2CH=$). ^{11}B NMR (neat substance), δ: 43.5.

Isomerization of *trans*-2,5-diallyl-1-(diallylboryl)pyrrolidine (22) into *cis*-2,5-diallyl-1-(diallylboryl)pyrrolidine (23). In a two-neck flask equipped with a thermometer, a reflux condenser, and an argon inlet, aminoborane **22** (6.84 g, 28.1 mmol) was placed and heated on an oil bath for 3 h at 185—195 °C. The ratio of aminoboranes **23** : **22** ≈ 3 : 1 was determined from the ^{13}C NMR spectra. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.65—2.2 (m, 10 H, $-CH_2-$); 2.35—2.5 (m, 2 H, CH_2);

3.75—3.9 (m, 2 H, HCN); 4.8—5.15 (m, 8 H, CH_2=); 5.6—6.05 (m, 4 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 26.95 (B—CH_2—); 29.67 (C(3), C(4)); 43.45 (—CH_2— in All); 58.95 (HCN); 113.41 (B—CH_2CH=CH_2); 116.37, 116.49 (C(4′), C(7′)); 135.76, 135.90 (C(3′), C(6′)); 137.19 (B—CH_2CH=).

***cis*-2,5-Diallylpyrrolidine (21).** To a mixture of isomers **22** and **23** (in a 1 : 3 ratio) resulting from isomerization **22** → **23** (see above), dry ether (10 mL) and 20% NaOH (8.5 mL) were added sequentially. The solution was stirred for 2 h and extracted with ether. The ethereal fractions were washed with saturated NaCl solution and dried (K_2CO_3), the solvents were evaporated, and distillation gave 3.13 g (74%) of a mixture of isomers **21** and **3**, b.p. 64—65 °C (7 Torr). The ratio **21** : **3** = 3 : 1 was determined from the ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.25—1.45 (m, **21** + **3**: $H(3)_a$, $H(4)_a$); 1.70—1.95 (m, **21** + **3**: NH, H(3), H(4)); 2.05—2.3 (m, **21** + **3**: —CH_2— in All); 2.95—3.12 (m, **21**: HCN); 3.13—3.3 (m, **3**: HCN); 4.9—5.1 (m, **21** + **3**: CH_2=); 5.65—5.9 (m, **21** + **3**: —CH=). ^{13}C NMR ($CDCl_3$), δ: 30.63 (**21**: C(3), C(4)); 31.2 (**3**: C(3), C(4)); 40.71 (**21**: —CH_2— in All); 41.14 (**3**: —CH_2— in All); 56.73, 56.90 (**3**: HCN); 58.43 (**21**: HCN); 116.22 (CH_2=); 136.17 (—CH=).

***cis*-2,5-Diallyl-1-acetylpyrrolidine (24).** A mixture of amines **18** and **24** (1 g, 90%) in a 1 : 3 ratio was obtained analogously to the synthesis of compound **18** from a mixture of amines **3** and **21** (0.87 g, 5.75 mmol, the **3** : **21** ratio was 1 : 3), prepared by isomerization **3** → **21**, and acetic anhydride (0.82 mL, 0.89 g, 8.7 mmol). *trans*-Isomer **18** was isolated on a column with SiO_2 (with ether as eluent). Distillation gave 0.64 g (64% with respect to the initial mixture of **3** and **21**) of acetate **24**, b.p. 94—95 °C (1 Torr), n_D^{19} 1.4914. Found (%): C, 74.81; H, 10.00; N, 7.34. $C_{12}H_{19}NO$. Calculated (%): C, 74.57; H, 9.91; N, 7.25. MS (EI, 70 eV), *m*/*z* (I_{rel}): 193 $[M]^+$ (4%), 192 $[M - H]^+$ (3%), 152 $[M - C_3H_5]^+$ (24%), 151 $[M - CH_2{=}C{=}O]^+$ (43%), 110 $[M - (C_3H_5 + CH_2{=}C{=}O)]^+$ (100%), 93 $[M - (C_3H_5 + MeCONH_2)]^+$ (22%), 81 $[M - (C_3H_5 + MeCO + CHNH)]^+$ (18%), 69 $[M - (2\ C_3H_5 + CH_2{=}C{=}O)]^+$ (24%), 68 $[M - (2\ C_3H_5 + MeCO)]^+$ (32%), 67 $[M - (C_3H_5 + C_3H_6 + MeCO)]^+$ (33%). IR (neat liquid), ν/cm^{-1}: 3450 (br), 3070, 2970, 2880, 1830, 1640, 1410, 1355, 1205, 1190, 1165, 1060, 1035, 1000, 920, 630, 550. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.65—2.45 (m, 10 H, H(3), H(4), Me, H(5′), $H(2')_b$); 2.65—2.8 (m, 1 H, $H(2')_a$); 3.7—3.9 (m, 1 H, H(5)); 3.95—4.15 (m, 1 H, H(2)); 4.95—5.15 (m, 4 H, CH_2=); 5.6—5.85 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 22.71 (Me); 27.95 (C(4)); 28.88 (C(3)); 39.06 (C(5′)); 39.94 (C(2′)); 57.14 (C(5)); 59.07 (C(2)); 116.93 (C(7′)); 117.81 (C(4′)); 134.23 (C(6′)); 134.87 (C(3′)); 169.32 (C=O).

Mixture of 5-allyl-2-pyrroline (25) and 2-allyl-3-pyrroline (4). A mixture of 1.43 g (7 mmol) of aminoboranes **1b** + **2b** (see above) was placed in a distillation flask in an argon stream and triethanolamine (1.57 g, 1.4 mL, 10.5 mmol) was added. The mixture of amines **25** and **4** (0.59 g, 78%) with b.p. 48—51 °C (12 Torr) was distilled off at a reduced pressure (water pump) on heating on a water bath. The ratio **25** : **4** = 65 : 35 was determined from the ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.3—1.6 (m, **25**: $H(4)_a$); 1.85—2.05 (m, **25**: $H(4)_b$); 2.1—2.65 (m, **25**: H(3), —CH_2— in All; **4**: —CH_2— in All, NH); 3.65—3.85 (m, **4**: CH_2N), 3.95—4.20 (m, **25**: H(5); **4**: H(2)); 4.95—5.2 (m, **25** + **4**: CH_2=); 5.6—6.0 (m, **25**: —CH= in All; **4**: —CH=); 7.5—7.65 (m, **25**: N=CH). ^{13}C NMR ($CDCl_3$), δ: 25.54 (**25**: C(4)); 36.43, 40.12 (**25**: C(3), —CH_2— in All); 40.88 (**4**: —CH_2— in All); 53.31 (**4**: C(5)); 64.29 (**4**: C(2)); 72.03 (**25**: C(5)); 116.21 (**25**: CH_2=); 116.44 (**4**: CH_2=); 128.34 (**4**: C(4)); 131.49 (**4**: C(3)); 135.16 (**25** + **4**: —CH= in All); 165.67 (**25**: C(2)).

Mixture of *trans*-2-allyl-5-butylpyrrolidine (26a) and *cis*-2-allyl-5-butylpyrrolidine (27a). To a mixture of 1.05 g (9.6 mmol) of amines **25** and **4** (in a 65 : 35 ratio) obtained from a mixture of aminoboranes **1b** and **2b** (see above), dry ether (15 mL) was added. At −60 °C, 6 mL of 1.78 *N* Bu^{n}Li solution in hexane (10.68 mmol) was added dropwise to the solution and the mixture was stirred for 4 h at this temperature. After 15 h, MeOH (1.3 L) was added to the solution at −30 °C; the mixture obtained was stirred for an additional 2 h, extracted with ether, and dried (K_2CO_3). After removal of the solvents and amine **4** at a reduced pressure (water pump), 0.83 g (79% with respect to the initial **25**) of a mixture of amines **26a** and **27a** was obtained, n_D^{20} 1.4681. The ratio of isomers **26a** : **27a** = 3 : 2 was determined from the ^{1}H and ^{13}C NMR spectra. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 127 $[M - C_3H_4]^+$ (30%), 126 $[M - C_3H_5]^+$ (100%), 110 $[M - C_4H_9]^+$ (14%), 109 $[M - C_4H_{10}]^+$ (91%), 68 $[M - (C_3H_{10} + C_4H_{10})]^+$ (38%). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.75—1.05 (m, **26a** + **27a**: Me); 1.1—1.6 (m, **26a** + **27a**: H(1), H(2) in Bu, H(3), H(4) in cycle); 1.75—2.35 (m, **26a** + **27a**: H(3) in Bu, H(2′), NH); 2.9—3.35 (m, **26a** + **27a**: NCH); 4.95—5.2 (m, **26a** + **27a**: CH_2=); 5.65—5.9 (m, **26a** + **27a**: —CH=). ^{13}C NMR ($CDCl_3$), δ: 13.98 (Me); 22.75 (C(1) in Bu); 29.41 (**26a**: C(2) in Bu); 29.59 (**27a**: C(2) in Bu); 30.57, 31.20 (**26a**: C(3), C(4) in cycle); 31.53, 32.07 (**27a**: C(3), C(4) in cycle); 36.25 (**27a**: C(3) in Bu); 36.74 (**26a**: C(3) in Bu); 40.65 (**27a**: C(2′)); 41.10 (**26a**: C(2′)); 56.94, 57.62 (**26a**: CN); 58.35, 59.24 (**27a**: CN); 116.21 (**27a**: CH_2=); 116.29 (**26a**: CH_2=); 136.1 (**27a**: —CH=); 136.19 (**26a**: —CH=).

Mixture of *trans*-2-allyl-5-phenylpyrrolidine (26b) and *cis*-2-allyl-5-phenylpyrrolidine (27b). To a mixture of 1.63 g (14.9 mmol) of amines **25** and **4** (in a 65 : 35 ratio) obtained from aminoboranes **1b** + **2b** (see above), dry ether (30 mL) was added and then 15.6 mL of 1.1 *N* ethereal PhLi solution (17.2 mmol) was added at −30 °C. The combined solution was stirred for 1 h at 0 °C and allowed to stay overnight. Then, EtOH (2 mL) was added to the solution at −20 °C and the mixture was stirred for 2 h, extracted with ether, and dried (K_2CO_3). After removal of the solvents and amine **4** at a reduced pressure (water pump), 1.11 g (61% with respect to the initial **25**) of a mixture of amines **26b** and **27b** was obtained, b.p. 94—95 °C (1 Torr), n_D^{20} 1.5310. The ratio of **26b** and **27b** (78 : 22) was determined from the ^{1}H and ^{13}C NMR spectra. MS (EI, 70 eV), *m*/*z* (I_{rel}): 186 $[M - H]^+$ (24%), 146 $[M - C_3H_5]^+$ (52%), 109 $[M - C_6H_6]^+$ (100%), 91 $[C_7H_7]^+$, 68 $[M - (C_3H_5 + C_6H_6)]^+$ (43%). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.54 (m, **26b**: $H(3)_a$; **27b**: $H(3)_b$); 1.55—1.83 (m, **26b**: $H(4)_a$; **27b**: $H(4)_b$); 1.86 (m, **27b**: $H(3)_a$); 2.03—2.21 (m, **26b**: $H(3)_b$; **27b**: $H(4)_a$); 2.22—2.39 (m, **26b**: $H(4)_b$; **26b** + **27b**: CH_2 in All, NH); 3.27 (m, **27b**: H(2)); 3.49 (m, **26b**: H(2)); 4.16 (t, **27b**: H(5)); 4.31 (t, **26b**: H(5)); 4.9—5.2 (m, **26b** + **27b**: CH_2=); 5.65—5.95 (m, **26b** + **27b**: —CH= in All); 7.05—7.45 (m, **26b** + **27b**: Ph). ^{13}C NMR ($CDCl_3$), δ: 30.52 (**27b**: C(3)); 31.65 (**26b**: C(3)); 30.60 (**27b**: C(4)); 34.74 (**26b**: C(4)); 40.75 (**27b**: C(2′)); 41.04 (**26b**: C(2′)); 57.39 (**26b**: C(2)); 58.07 (**27b**: C(2)); 60.79 (**26b**: C(5)); 62.07 (**27b**: C(5)); 115.94 (**27b**: CH_2=); 116.27 (**26b**: CH_2=); 125.95, 126.23, 126.33, 127.93 (**26b** + **27b**: Ph); 135.75 (**26b**: —CH= in All); 135.94 (**27b**: —CH= in All); 144.52 (**27b**: C_i); 145.39 (**26b**: C_i).

Formation of adduct of boron trifluoride with 2*H*-pyrrole (34). To 0.45 mL (3.7 mmol) of $Et_2O \cdot BF_3$ (distilled over CaH_2), pyrrole (0.37 mL, 5.4 mmol) and $CDCl_3$ (0.37 mL) were added. The content of pyrrole (~ 90%) and adduct **34** (10—12%) was determined from the ^{1}H NMR spectrum of the mixture. **Adduct 34**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.63 (m,

2 H, H(5)); 6.56 (m, 1 H); 7.67 (m, 1 H); 8.45 (m, 1 H). ^{13}C NMR ($CDCl_3$), δ: 63.04 (C(5)); 127.65 (C(4)); 155.50 (C(3)); 169.3 (C(2)).

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References

1. Yu. N. Bubnov, V. C. Bogdanov, and B. M. Mikhailov, *Zh. Obshch. Khim.*, 1968, **38**, 260 [*J. Gen. Chem. USSR*, 1968, **38** (Engl. Transl.)].
2. A. Meller and G. Gerger, *Monatsh. Chem.*, 1974, **105**, 684.
3. R. W. Hoffmann, G. Eichler, and A. Endesfelder, *Lieb. Ann. Chem.*, 1983, 2000.
4. Y. Yamamoto, S. Nishii, K. Maruyama, T. Kamatsu, and W. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 7778.
5. Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.
6. Yu. N. Bubnov, V. I. Zheludeva, T. Yu. Rudashevskaya, and T. S. Kuznetsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1179 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1073 (Engl. Transl.)].
7. L. I. Lavrinovich, A. V. Ignatenko, and Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2597 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2051 (Engl. Transl.)].
8. M. E. Gurskii, S. B. Golovin, A. V. Ignatenko, and Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2198 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1724 (Engl. Transl.)].
9. Yu. N. Bubnov, S. V. Evchenko, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2815 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2239 (Engl. Transl.)].
10. 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.)].
11. Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1203 [*Russ. Chem. Bull.*, 1995, **44**, 1156 (Engl. Transl.)].
12. Yu. N. Bubnov, *Pure Appl. Chem.*, 1994, **66**, 235.
13. Yu. N. Bubnov, L. I. Lavrinovich, A. Yu. Zykov, E. V. Klimkina, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1327 [*Russ. Chem. Bull.*, 1993, **42**, 1269 (Engl. Transl.)].
14. Yu. N. Bubnov, A. Yu. Zykov, L. I. Lavrinovich, and A. V. Ignatenko, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1329 [*Russ. Chem. Bull.*, 1993, **42**, 1271 (Engl. Transl.)].
15. R. A. Jones, in *Comprehensive Heterocyclic Chemistry*, Eds. A. R. Katritzky and W. Rees, Pergamon Press, Oxford, 1984, **4**.
16. A. H. Jackson, in *Comprehensive Organic Chemistry*, Eds. D. Barton and W. D. Ollis, Pergamon Press, Oxford—New York—Toronto—Sydney—Paris—Frankfurt, 1979, **4**.
17. R. Köster, H. Bellut, and S. Hattori, *Lieb. Ann. Chem.*, 1968, **720**, 1.
18. H. Bellut and R. Koster, *Lieb. Ann. Chem.*, 1970, **738**, 86.
19. R. R. Hill and T. H. Chan, *Tetrahedron*, 1965, **21**, 2015.
20. 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.)].
21. 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.)].
22. Yu. N. Bubnov, E. V. Klimkina, A. V. Ignatenko, and I. D. Gridnev, *Tetrahedron Lett.*, 1997, **38**, 4631.
23. Yu. N. Bubnov, E. V. Klimkina, A. V. Ignatenko, and I. D. Gridnev, *Tetrahedron Lett.*, 1996, **37**, 1337.
24. S. M. Bachrach, *J. Org. Chem.*, 1993, **58**, 5414.
25. T. A. Zawodzinski, Jr., L. Janiszewska, and R. A. Osteryoung, *J. Electroanal. Chem.*, 1988, **255**, 111.

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