Reductive *trans*-2,6-diallylation of pyridines with allylboranes. Synthesis of *trans*- and *cis*-2,6-diallyl-1,2,5,6-tetrahydropyridines and their deuterated derivatives

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The reductive *trans*-2,6-diallylation of pyridines with triallyl- and allyl(dialkyl)boranes has been discovered. Heating (40—100 °C) of pyridine, deuteropyridine, or 3-bromopyridine complexes with triallylborane in the presence of alcohols (ROH or CH_3OD), water, or Et_2NH results in the respective *trans*-2,6-diallyl-1,2,5,6-tetrahydropyridines (**2**, **3**, **22**, or **25**) in 20—97 % yields. A preparative method for the isomerization of *trans*-2,6-diallyl compounds **2** and **25** into the respective *cis*-isomers **4** and **28** by heating them with triallyl- or allyl(dialkyl)boranes (125—150 °C) has been suggested. The hydrogenation of *trans*- or *cis*-2,6-diallyl-1,2,5,6-tetrahydropyridines gave *trans*- or *cis*-2,6-dipropylpiperidines, respectively. The *cis*- and *trans*-configurations of compounds **2** and **4** were established by analyzing the NMR spectra of *N*-benzyl (**7** and **13**) and *N,N*-dimethyl (**6** and **14**) derivatives of piperidine derivatives **5** and **8**. A possible mechanism for the reductive diallylation of pyridines has been discussed.

Key words: allylboranes; triallylborane complexes; allylboration; pyridines; reductive *trans*-2,6-diallylation of pyridines; *cis*- and *trans*-diallyl-1,2,5,6,-tetrahydropyridines; *cis*- and *trans*-2,6-dipropylpiperidines; *trans*-*cis*-isomerization.

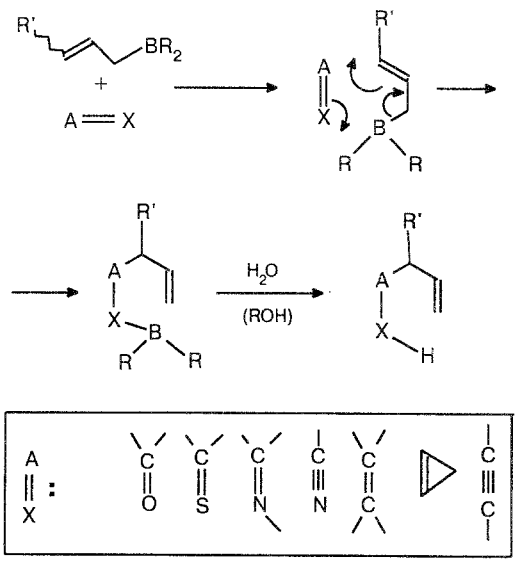
β,γ-Unsaturated (allylic) boron derivatives add to aldehydes, ketones, thioketones, imines, nitriles, acetylenes, and certain olefins.[1—5] The more strongly a multiple bond is polarized or strained,[4] the more easily the addition occurs.

All allylboration reactions proceed regio- and stereospecifically, likely *via* a chair-like six-centered transition state (the $2\pi+2\pi+2\sigma$-process).[1,3,5,6] Allylboration has already been used for over twenty years as the key step in the syntheses of organic compounds of various classes, including many natural compounds and their analogs.[1b,3,4]

In the case of carbonyl compounds, imines, and thioketones, allylboration proceeds by the classical scheme of organometallic synthesis (Scheme 1).

On the other hand, it is well known that organomagnesium and -lithium compounds add to pyridine at the 1,2- and/or 1,4-positions.[6—10] The addition products are usually unstable and readily undergo oxidation (or elimination of MH) to give 2- and 4-alkyl(aryl)pyridines upon standard treatment of the reaction mixture. The reactions of pyridine with excess RLi give 2,4- and 2,6-dialkylpyridines.[6,8] The reaction with excess *tert*-butyllithium results in 2,4,6-tri-*tert*-butylpyridine along with other products.[6,8,10] We know only one exception. Francis *et al.*[10,11] treated a mixture of pyridine and a 5—10-fold molar excess of *t*-BuLi with methanol

Scheme 1



(−70 °C) and obtained three main products: 2-*tert*-butylpyridine (~27 %), 2-*tert*-butyl- (~22 %), and *trans*-2,6-di-*tert*-butyl-1,2,3,6-tetrahydropyridine (THP) (40—55 %). Although the reaction proceeds ambigously to give a mixture of compounds, the formation of THP

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is, to our knowledge, the only example of the reductive 2,6-dialkylation of pyridine with an organometallic compound. The hydrogenation of THP afforded *trans*-2,6-di-*tert*-butylpiperidine.[11]

Pyridinium salts also add organometallic compounds (RMgX, RLi, RZnX, $R_3Al_2X_3$, RCu, $RLi \cdot BF_3$, $BuLi \cdot BBu_3$, $BuMgBr \cdot BBu_3$, *etc.*) at the 1,2- or 1,4-positions, and the direction of these reactions is determined by the nature of the quaternizing group and the organometallic nucleophile.[6,8,12–16] In some cases, high 1,2- or 1,4-regioselectivity is observed.[12–16] It is also known that the $Py \cdot BF_3$ complex is readily metallated by lithium 2,2,6,6-tetramethylpiperidide at the α-position,[17] and the reaction of allyltrimethylsilane with pyridine *N*-oxides results in 2-(1-propenyl)pyridines.[18] Alkoxycarbonylpyridinium salts react with allylstannanes (but not with allylsilanes) to give 2-allyl-1,2-dihydropyridines.[19] Allylic zinc derivatives add to the vinyl group of 2-vinylpyridine.[20]

In a continuation of the investigations into the allyl-type boron compounds[4,5,21,22] we studied the transformations of pyridine and some of its derivatives by the action of triallylborane under nonstandard but very simple conditions. As a result, we discovered a new general, regio- and stereospecific reaction, which was called **the reductive *trans*-2,6-diallylation of pyridines.** This remarkable reaction is accompanied by a "violation of aromaticity" (for a preliminary communication *cf.* Ref. 23).

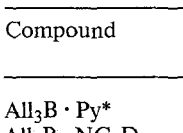
Results and Discussion

Triallylborane and pyridine form a stable complex **1** which can be distilled *in vacuo* (Table 1).

This complex has been obtained and studied by many chemists.[24–27] For example, its IR, Raman,[27] and NMR spectra[25,26] have been studied. According to the data in Ref. 26, the dissociation energy of complex **1** is *ca.* 15 kcal mol^{-1}.

We found that complex **1** does not change during prolonged heating (160 °C, 20 h). In this study we also obtained complexes of triallylborane with deuteropyridine and 3-bromopyridine, which are stable in an inert atmosphere (Table 1).

Table 1. Complexes of triallylborane with pyridine and its derivatives

Compound	B.p./°C (*p*/Torr)	n_D^{20}	$\delta^{11}B$,
$All_3B \cdot Py$*	102 (1)	1.5435[26]	0
$All_3B \cdot NC_5D_5$	103—104 (1)	1.5409	−0.60
	106 (1)	1.5643	−0.3

* d_4^{20} 0.932; μ = 4.97 D;[26] m.p. 14—15 °C (our data).

Reductive diallylation of pyridine

We found that the treatment of complex **1** with water, alcohols, or amines (Et_2NH) results in its complete rearrangement to give *trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine (**2**). The yield of compound **2** is 20—97 %, depending on the reaction conditions (Table 2), and has the maximum value (97 %) if complex **1** is heated (95—100 °C) with four equivalents of isopropanol in the presence of pyridine (1 mol) (Scheme 2).

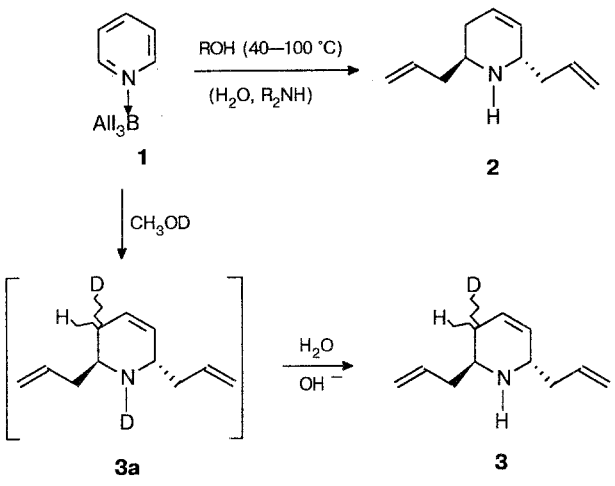
The successive treatment of complex **1** with monodeuteromethanol (46 °C, 4 h) and 10 % NaOH gave *trans*-2,6-diallyl-5-deutero-1,2,5,6-tetrahydropyridine **3** in 78 % yield. Undoubtedly, the 1,5-dideuterated compound **3a** is initially formed and is transformed to **3** on shaking with an alkali (the replacement of N—D by N—H).

Table 2. Effect of the reaction conditions on the yield of *trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine **2**[a]

ROH (R_2NH)	T/°C	Solvent	τ/h	Yield (%)
MeOH	40—60	Ether	2—6	35—50
MeOH	20	THF	96	57
MeOH	80	Benzene	4	43
MeOH[b]	45	Ether	4	57—63
MeOH[c]	40	Ether	2	34
MeOH[d]	40	Ether	2	24
MeOH[e]	45	Ether	4	40
MeOH[f]	45	Ether	2	40
EtOH	60	Ether	3	50
EtOH	85	—	4	53
EtOH[b]	45	Ether	4	60
i-PrOH	45	—	2	63
i-PrOH	90	—	8	70
i-PrOH[b]	100	—	2	97
t-BuOH	95	—	6	85[i]
t-BuOH	95	—	8	92[i]
$(CH_2OH)_2$	90	—	6	36
Et_2NH	70	—	2	21
Et_2NH	70	—	16	23
H_2O	40	THF	8	40
H_2O	50	—	3	76[j]
10 % NaOH	45	—	2	5
1.4:3.6-Dianhydro-D-mannitol[g]	55	Hexane	5	70
(−)-Menthol[h]	45	Ether	10	66

[a] The typical ratio triallylborane : pyridine : ROH (H_2O or Et_2NH) = 1:1:4. [b] The ratio triallylborane : pyridine : alcohol = 1:2:4. [c] MeOH (2 mol) was used. [d] MeOH (1 mol) was used. [e] Allyl(dipropyl)borane was used instead of triallylborane. [f] A mixture of triallylborane, $CH_2{=}CHCH_2B(OMe)_2$, pyridine and the alcohol in the 1:1:1.1:4 ratio was used. [g] The product **2** obtained has $[\alpha]_D^{23}$ +4.38° (*c* = 10.28; CH_2Cl_2). [h] The product **2** obtained has $[\alpha]_D^{23}$ −7.30° (*c* = 10.00; CH_2Cl_2). [i] A 9—10 % admixture of the *cis*-isomer. [j] A 6 % admixture of the *cis*-isomer.

Scheme 2



The reductive *trans*-2,6-diallylation of pyridines can be performed in any inert solvent (ether, THF, benzene, hexane, chloroform, CCl_4, excess pyridine, *etc.*). However, it is more convenient to use no solvent at all. At least two equivalents of an alcohol, water, or amine should be taken. Evidently, the optimum amount of alcohol is four equivalents, since it is also consumed by a side process, *viz.*, protolytic cleavage of one B—C bond of triallylborane with the liberation of propylene.[1] If compound **1** is heated with isopropanol or *tert*-butanol, the protolysis practically does not take place, which increases the yield of **2** (see below).

It is convenient to monitor the progress and completion of the reaction by recording the IR spectra, *i.e.*, watching the decrease in the intensity of the bands corresponding to the double bonds in complex **1** (1625 and 1630 cm^{-1}) and the appearance and growth of a band at 1642 cm^{-1} due to terminal double bonds of product **2**. When the process is completed, the reaction mixture is treated with 10 % NaOH (1.2—1.5 equivalents of alkali per one equiv. of the starting allylborane) transferring all boron compounds (allyl- and diallylboric acids) into the aqueous layer as the borate, while product **2** is extracted with ether and distilled *in vacuo*.

Amine **2** can also be isolated from the reaction mixture in another way, namely, by adding mono- or triethanolamine (fixing the boron compounds) followed by extraction by petroleum ether or evaporation of **2** *in vacuo*.

Oxidation with hydrogen peroxide in an alkaline medium or treatment of the reaction mixture with an ethereal or aqueous HCl solution are also efficient but less convenient from the experimental viewpoint.

The yield of compound **2** depends markedly on the nature of the protolytic reagent used and the reaction conditions (Table 2). In the presence of most alcohols (4 equivalents) and diols, the reductive diallylation of complex **1** is completed in 2—4 h, and the yield of **2** is 40—70 %. The best results were obtained by heating **1** with 4 equiv. of isopropanol at 90—100 °C, but the reaction with this alcohol proceeds 1.5—2 times more slowly than with methanol or ethanol.

If excess pyridine is used, the protolytic cleavage of trialkylborane is suppressed, since the equilibrium

$$All_3B \cdot Py \rightleftharpoons All_3B + Py$$

is shifted to the left, and the yield of **2** increases. For example, boiling a mixture of triallylborane, pyridine, and isopropanol in the ratio 1 : 2 : 4 (98 °C, 2 h) gives amine **2** in 97 % yield, while if the ratio is 1 : 1 : 4 (98 °C, 2 h), the yield is 70 %.

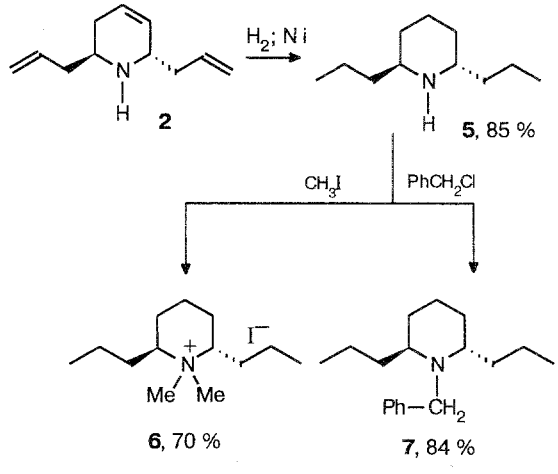
trans-2,6-Diallyl-1,2,5,6-tetrahydropyridine **2** obtained in different experiments contains 1—2 % of an admixture of *cis*-isomer **4** (GLC). In some experiments with *t*-BuOH (4 equiv., 95—100 °C), the admixture of the *cis*-isomer reached 9—10 %, and that obtained with water reached 6 %. The admixture of *cis*-isomer **4** is easily separated chromatographically by passing the hexane solution through a column with a small amount of SiO_2 (when its content is 1—2 %) or by column distillation (20 theoretical plates).

Compound **2** is a colorless liquid which turns yellow on storage. Its structure was established by a combination of chemical and physicochemical methods (IR, ^1H and ^{13}C NMR, and mass spectroscopy).

The IR spectrum of the pure compound contains intense absorption bands at 1642, 1650 (sh), 3030, and 3079 cm^{-1} (CH_2=CH and CH=CH) along with broad bands at 3280 and 3330 cm^{-1} (NH).

The ^1H NMR spectrum ($CDCl_3$) displays multiplets at δ 2.90 (1 H, H-6), 3.35 (1 H, H-2), 5.0 (4 H, CH_2=C), and 5.6 (4 H, C=CH—, CH=CH). The ^{13}C NMR spectrum contains 11 signals. The mass spectrum (electron impact) displays intense peaks at 122 [M−C_3H_5], 80 [M−2C_3H_5], and 41 [C_3H_5]. Chemical ionization (CH_4) gives intense peaks at 164.1587 ([MH]$^+$,

Scheme 3



13.9 %), 162.2013 ([M−H], 2.3 %), 122.1357 ([M−C_3H_5], 100 %).

The hydrogenation of compound **2** in acetic acid over Raney nickel in an autoclave (90—100 °C, 100 atm. of H_2, 6 h) resulted in *trans*-2,6-dipropylpiperidine **5** (yield 85 %), which was transformed to *N,N*-dimethyl salt **6** (70 %) or *N*-benzyl derivative **7** (84 %) by the action of methyl iodide[28] or benzyl chloride,[29] respectively.

Both methyl groups in salt **6** are equivalent: one signal in the ^{1}H NMR spectrum (δ 3.38, 6 H) and one in the ^{13}C spectrum (δ 49.02) are observed. The methylene protons (CH_2Ph) in the ^{1}H NMR spectrum of *N*-benzyl compound **7** appear as an AB-system with the quartet centered at δ 3.66 (δ_A 3.60, δ_B 3.70; J = 14.04 Hz), which indicates their chemical nonequivalence (diastereotopticity). These data imply unambiguously the *trans*-arrangement of the propyl groups with respect to the ring in the piperidine derivatives (**5**—**7** and **5** • **HCl**)

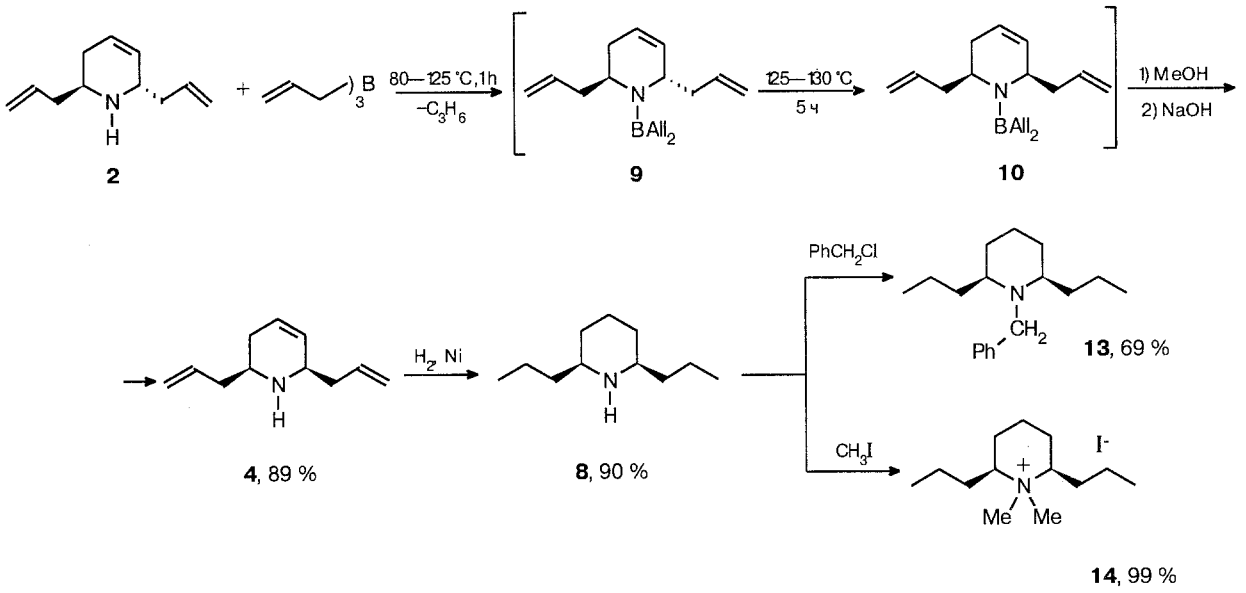
Table 3. Isomerization of *trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine **2** into *cis*-isomer **4** by heating with triallylborane

T/°C	Duration of heating/h	Yield (%)	Amount of the *trans*-isomer (%)
100—120	2	80	22
120—130	2.5	81	9
120—130	4	84	4
125—130	5	85	2.5
125—130	15	89	1.5

and, hence, prove the *trans*-stereochemistry of 2,6-diallyl compound **2**.

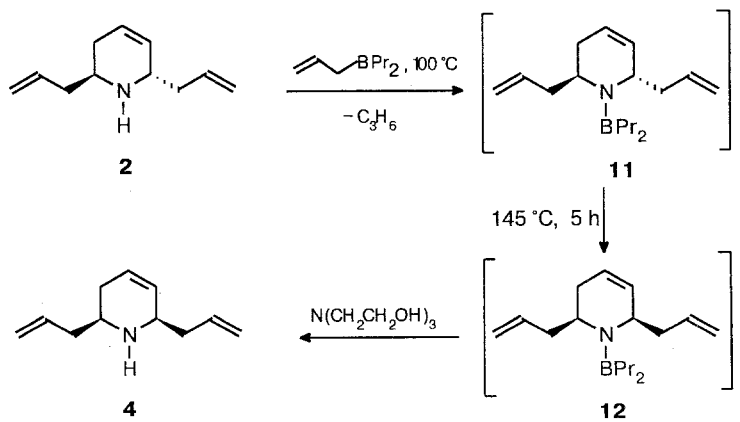
^{1}H NMR spectra of this type have been observed previously in the case of the *N,N*-dimethyl salt of *trans*-2,6-dimethylpiperidine[30] and the *N*-benzyl derivative of the latter.[31]

Scheme 4



2 **9** **10** **13**, 69 % **4**, 89 % **8**, 90 % **14**, 99 %

Scheme 5



2 **11** **12** **4**

It was also desirable to obtain *cis*-2,6-diallyl-1,2,5,6-tetrahydropyridine (**4**) and *cis*-2,6-dipropylpiperidine (**8**).

trans-cis Isomerization of 2,6-diallyl-Δ^3-piperideine

We found a method (for the preliminary communication see Ref. 32) for the practically quantitative isomerization of *trans*-compound **2** into the *cis*-isomer **4** by heating **2** with an equimolar amount of triallylborane at 125—130 °C (Table 3) or allyl(dipropyl)borane at 140—150 °C for 5—10 h (Schemes 4 and 5).

At the first stage of the reaction with triallylborane, one B—C bond in the latter is cleaved[1] to give one mole of propene and aminoborane **9**, which is transformed to isomeric compound **10** on subsequent heating (125—130 °C). The latter was not isolated as an individual compound but was deboronated at once by the action of methanol (0—20 °C, cleavage of the B—N bond)[1] and 10 % NaOH (1.2 equiv.). The *cis*-2,6-diallyl-1,2,5,6-tetrahydropyridine **4** thus obtained contained 1.5—2.5 % of *trans*-isomer **2**. The latter is readily isolated by passing a pentane solution of the product through a column with SiO_2. The yield of pure **4** is about 80 %.

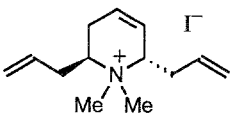
It turned out that not only tetraallyl compound **9** but also its *B,B*-dipropyl analog (**11**) undergo *trans-cis*-isomerization. For example, heating *trans*-compound **2** with allyl(dipropyl)borane (140—150 °C, 5 h) followed by deboronation of the resulting aminoborane (**12**) (Scheme 5) gave *cis*-compound **4** (the admixture of **2** was less than 5 %).

The hydrogenation of *cis*-isomer **4** (Ni, CH_3COOH, 100 °C, 100 atm. of H_2) resulted in *cis*-2,6-dipropylpiperidine **8** (90 %) which was used to obtain hydrochloride **8** · HCl (89 %), *N*-benzyl derivative **13** (70 %), and *N,N*-dimethyl salt **14** (99 %). As in *cis*-1,1,2,6-tetramethylpiperidinium iodide,[30] the methyl groups in salt **14** are nonequivalent and manifest themselves as two signals at δ 2.88 and 3.40 in the ^{1}H NMR spectrum as well as two signals at δ 37.24 and 48.69 in the ^{13}C NMR spectrum. The benzyl protons in compound **13** (NCH_2Ph) are chemically equivalent (enantiotopic) and are manifested in the ^{1}H NMR spectrum as a distinct singlet at δ 3.65. A similar picture was observed in the case of 1-benzyl-*cis*-2,6-dimethylpiperidine.[31]

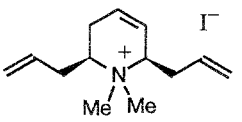
Thus, we have obtained new evidence that it is surprisingly easy to determine the stereochemistry of 2,6-disubstituted piperidines by using a prochiral *N*-benzyl probe and *N,N*-dimethyl quaternization.

We established that the ^{1}H NMR spectroscopy of *N*-benzyl derivatives can also be successfully used to determine the steric structure of some 2,6-dialkyl-1,2,5,6-tetrahydropyridines, in particular, 2,6-diallyl derivatives **2** and **4**, as well as their deutero- and bromo-substituted analogs (*vide infra*).

Heating *trans*- (**2**) and *cis*-isomer (**4**) with CH_3I or benzyl chloride in ethanol in the presence of K_2CO_3 gave *N,N*-dimethyl salts **15** (77 %) and **16** (89 %) and the respective *N*-benzyl derivatives **17** (92 %) and **18** (62 %).



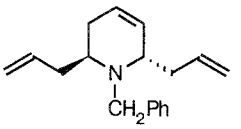
15, 77 %



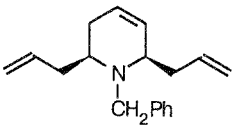
16, 89 %

^{1}H NMR: δ 3.38 3.51 Δδ 0.13 — δ 2.94 3.58 Δδ 0.64

^{13}C NMR: δ 47.67 48.59 Δδ 0.92 — δ 38.93 48.72 Δδ 9.79

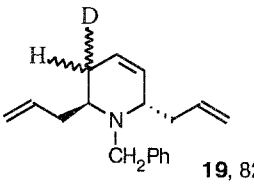


17, 92 %



18, 62 %

^{1}H NMR: δ_A 3.50, δ_B 3.70 (J_{AB} = 13.73 Hz), Δδ 0.20; δ 3.90 (singlet)



19, 82%

^{1}H NMR: δ_A 3.43, δ_B 3.67 (J_{AB} = 13.85 Hz), Δδ 0.24

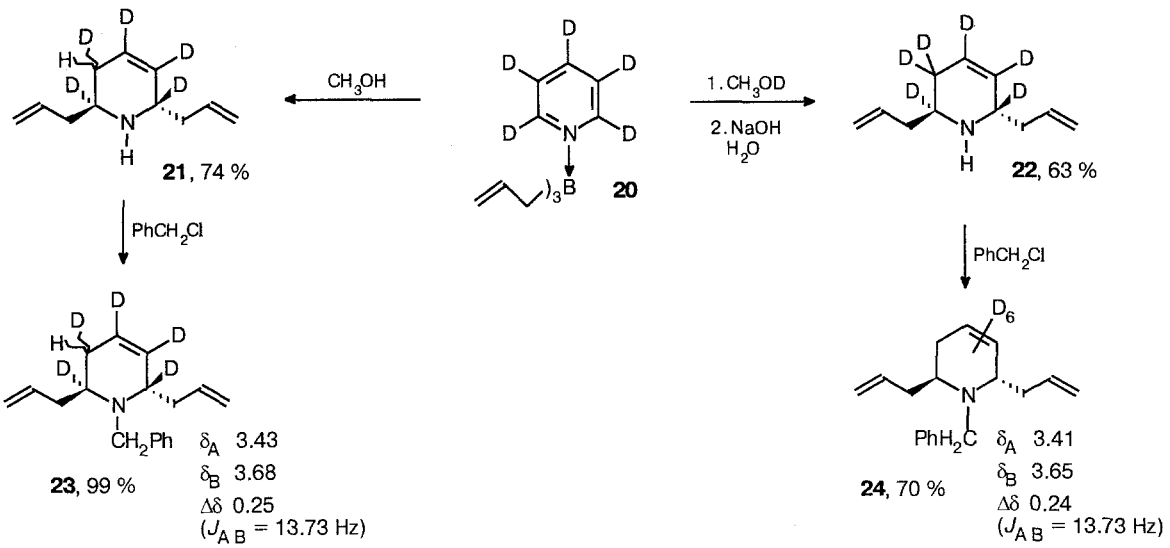
In the ^{1}H NMR spectrum of *N*-benzyl-*trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine **17**, the chemically non-equivalent benzyl protons (CH_2Ph) appear as an AB-system (δ_A 3.50, δ_B 3.70, J = 13.73 Hz) with a center at δ 3.60, while the spectrum of *cis*-isomer **18** displays a distinct singlet at δ 3.90 (CH_2Ph).

On the other hand, the ^{1}H NMR spectra of each of the *N,N*-dimethyl salts of *trans*-isomer **15** and *cis*-isomer **16** contain two singlets for methyl groups (at δ 3.38 and 3.51 for **15** and at δ 2.94 and 3.58 for **16**). One can easily see that the difference in the chemical shifts of the pseudoaxial and pseudoequatorial methyl groups of *trans*-isomer **15** (Δδ 0.13) is less than that for *cis*-isomer **16** (Δδ 0.64).

An even clearer picture was obtained when the ^{13}C NMR spectra of *N,N*-dimethyl salts **15** and **16** were compared. The difference in the chemical shifts (38.93 and 48.72 ppm) of the two nonequivalent methyl groups is much greater in the case of *cis*-isomer **16** (Δδ 9.79) than in the case of salt **15**, which has a *trans*-configuration of the allyl groups (δ 47.67 and 48.59, Δδ 0.92).

As was already mentioned (Scheme 2), heating complex **1** with deuteromethanol followed by treatment with 10 % NaOH (deboronation) results in compound **3** with

Scheme 6



a deuterium atom at position 5. This was then transformed to hydrochloride **3** · HCl (98 %) and benzyl derivative **19** (82 %), the ^{1}H NMR spectrum of which contains a doublet of doublets of the AB-system (δ_A 3.43, δ_B 3.67, J = 13.85 Hz, CH_2Ph).

Reductive diallylation of deuteropyridine and 3-bromopyridine

We then studied the reductive diallylation of deuteropyridine with triallylborane (complex **20**) by action of methanol and deuteromethanol (4 equiv.) to give pentadeuterated compound **21** (74 %) and *trans*-2,6-diallyl-2,3,4,5,5,6-hexadeutero-1,2,5,6-tetrahydropyridine **22** (63 %), respectively. We transformed these further to the respective *N*-benzyl compounds, **23** (99 %) and **24** (70 %). The chemical shifts for the nonequivalent protons of the CH_2Ph group (AB spectrum) in compounds **23** and **24** are given in Scheme 6.

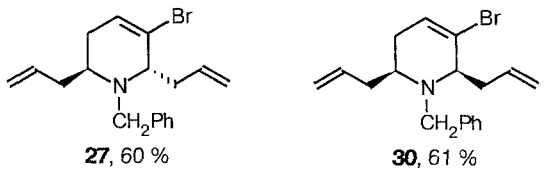
3-Bromopyridine also readily gives *trans*-2,6-diallylation product **25** (60—80 %), in which the bromine atom is bonded to the vinylic carbon atom.

When complex **26** is heated with methanol (4 equiv., 70 °C, 5 h), the yield of compound **25** is 64 %, or 72 % if the reaction is carried out in the presence of 0.5 equiv. of bromopyridine; the admixture of the *cis*-isomer is 1.5—1.7 %. The reaction of compound **26** with isopropanol (4 equiv., 95 °C, 6 h) gave **25** in 63 % yield (the admixture of the *cis*-isomer was 3.1 %). Amine **25** obtained in 83 % yield by boiling complex **26** with Bu^{t}OH (4 equiv., 98 °C, 5 h) contained 7.8 % of the *cis*-isomer (GLC).

Bromide **25** was transformed into *N*-benzyl derivative **27** and hydrochloride **25** · HCl. The structure of the latter was confirmed by an X-ray diffraction study (these data will be published in the next communication).

Like compound **2** (Scheme 2), *trans*-bromide **25** is transformed into *cis*-isomer **28** (yield 75 %) when heated with triallylborane (130 °C, 3 h) followed by deboronation of the aminoborane **29** not isolated in the individual state (Scheme 7). In this case, isomerization does not come to completion even after heating for 6 h. The product obtained contained *ca.* 6 % of *trans*-isomer **25**. The mixture was separated by chromatography on silica gel (pentane as the eluent). As a result, the chromatographically pure *cis*-isomer **28** was obtained.

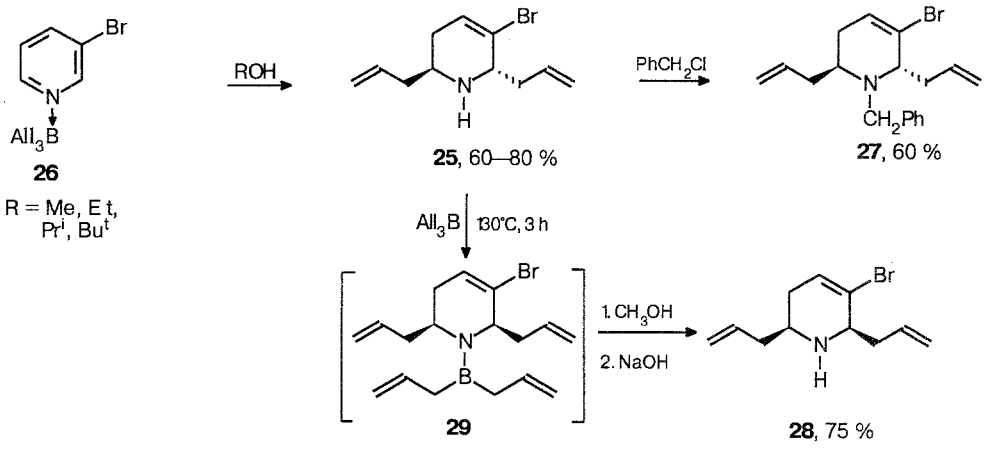
The nonequivalent benzyl protons of *trans*-isomer **27** (δ_A 3.48, δ_B 3.93, J = 13.70 Hz) and *cis*-isomer **30** (δ_A 3.67, δ_B 3.77, J_{AB} = 13.93 Hz) are manifested in the ^{1}H NMR spectra as an AB system. The difference in the chemical shifts (H_A and H_B) is much smaller for isomer **30** (Δδ 0.1) than for *trans*-compound **27** (Δδ 0.45).



^{1}H NMR, δ CH_2Ph	δ_A 3.48	δ_A 3.67
	δ_B 3.93	δ_B 3.77
	Δδ 0.45	Δδ 0.10
	(J_{AB} = 13.70 Hz)	(J_{AB} = 13.93 Hz)

As follows from the data presented above, the reductive *trans*-diallylation of pyridines has general applicability and can be used to obtain many *cis*- and *trans*-2,6-disubstituted Δ^3-piperideines and piperidines.

Scheme 7



A possible mechanism of reductive diallylation

Because complex **1** (as well as **20**) does not undergo any transformations at 160 °C (20 h), it is quite obvious that the alcohol (or water or R_2NH) plays a crucial role in this reaction. As seen from Schemes 2 and 6, a hydrogen (deuterium) atom from the alcohol is localized at positions 1 and 5 of the nitrogen-containing ring. However, the first step of the process is not quite clear yet.

As in pyridinium salts[6—8] and Py · BR_3 adducts (R = H, Me, Et),[33] the nitrogen atom in complex **1** is charged positively, which should favor a nucleophilic attack at the α-position of the ring. It is well known that pyridinium and quinolinium salts readily add alkoxide ions to give 2-alkoxy-1,2-dihydropyridines and 1,2-dihydroquinoline.[6—8,34] For example, the α-addition of a hydroxide ion is the key step in the well-known oxidation of pyridinium salts with an alkaline solution of potassium ferricyanide to give 2-pyridones.[6—8,35]

It can be assumed (Scheme 8) that initially a molecule of alcohol attacks the pyridinium cycle of complex **1** to give a nucleophilic addition product **31** or, more likely, **32**. Both of them contain a localized C=N bond which instantly undergoes allylboration *via* transition state **33**. As a result, aminoborane **34** is formed having a covalent B—N bond and an electronegative OR group at position 2 relative to the boron atom. The latter quickly undergoes β-elimination to give a new imine complex **35**.

The next step, *viz.*, allylboration of the second C=N bond, **occurs stereoselectively**, *i.e.*, by the addition of a second allylboron fragment at the ***trans*-position** with respect to the allyl group already bonded to the ring (transition state **36**). The B—N bond in the aminoborane **37** thus formed is immediately cleaved by the alcohol present in the reaction mixture (2—4 equiv.). As a result, *trans*-2,6-diallyl-Δ^3-piperideine **3a** is formed.

We considered a possible reaction mechanism involving compound **32**, the product of an alcohol 1,4-addition (at positions 2 and 5 of the pyridine ring of complex **1**). The general scheme does not change if adduct **31** is formed at the first step. However, we prefer the scheme involving compound **32** as the intermediate.

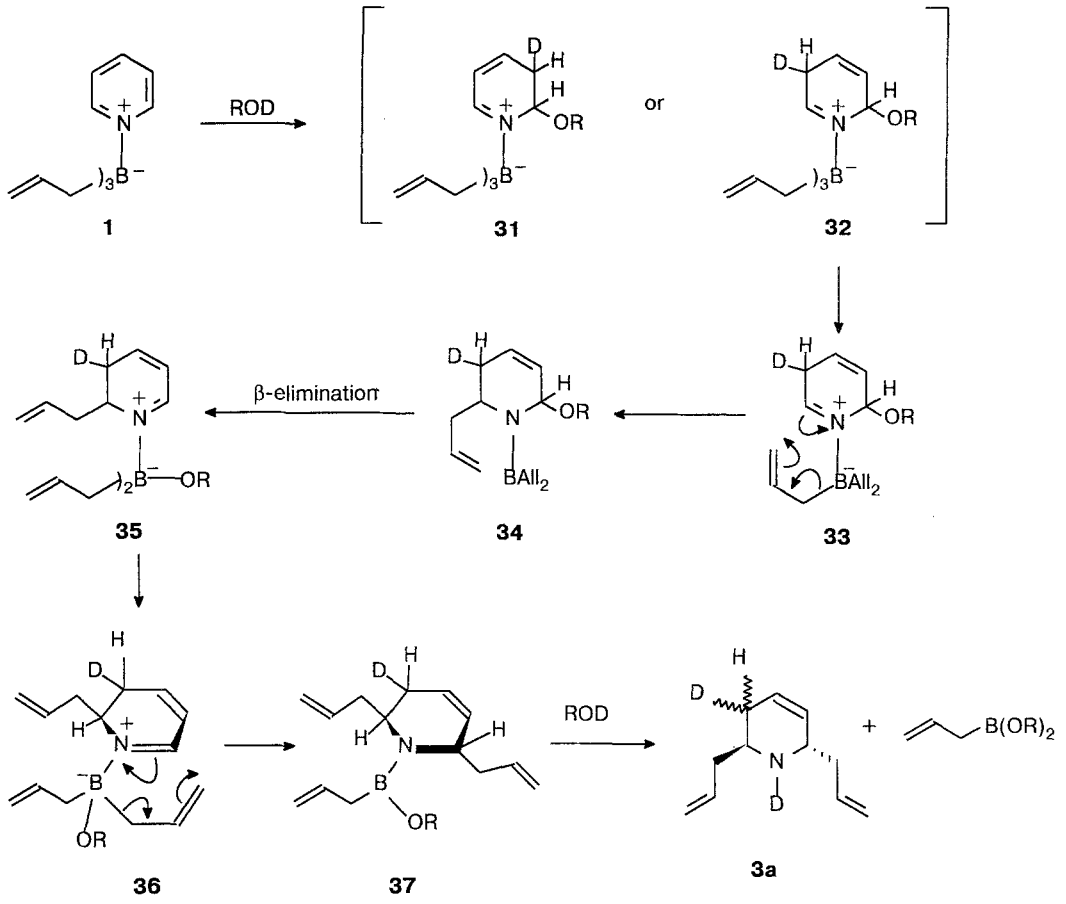
We established for the reaction of pyridine with tricrotylborane that the reductive *trans*-diallylation of pyridines (the addition of two allyl groups) is accompanied by allylic rearrangement.

Experimental

All operations with organoboron compounds were performed under dry argon. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer. The chemical shifts are given in the δ scale relative to TMS. ^{11}B NMR spectra were also recorded on a Bruker AC-200P spectrometer; the chemical shifts (δ) are given relative to $BF_3 \cdot OEt_2$. IR spectra were obtained on an UR-20 spectrophotometer. Mass spectra were obtained on Varian MAT and MS-30 spectrometers.

***trans*-2,6-Diallyl-1,2,5,6-tetrahydropyridine (2).** Triallylborane (10.2 g, 76 mmol) was placed into a three-necked flask equipped with a thermometer, a reflux condenser, and an argon inlet and connected with a gas burette *via* a condenser. Pyridine (12.2 mL, 152 mmol) was added with cooling (−70 °C), then isopropanol (23.3 mL, 304 mmol) was added at 0 °C. The reaction mixture was refluxed for 2 h at 98 °C; this was accompanied by evolution of propene (70 mL, 3 mmol). The reaction mixture was treated with 20 % NaOH (23 mL), extracted with ether (10—60 mL), and dried with K_2CO_3. Distillation gave 12.01 g (97 %) of compound **2**, b.p. 62—64 °C (2 Torr), $n_D^{22.5}$ 1.4880. Found (%): C, 80.87; H, 10.45; N, 8.61. $C_{11}H_{17}N$. Calculated (%): C, 80.92; H, 10.49; N, 8.58. MS (EI, 70 eV), *m/z*: 122 $[M-C_3H_5]^+$. IR ($CHCl_3$), ν/cm^{-1}: 1432, 1452, 1638 (sh. 1650), 3070 (—CH=CH_2 and CH=CH); 3300 (NH). ^1H NMR ($CDCl_3$), δ: 1.70 (m, 1 H, N—H); 1.80—2.23 (m, 6 H, CH_2—C=); 2.90 (m, 1 H, H-6); 3.35 (m, 1 H, H-2); 4.90—5.05 (4 H, CH_2=C); 5.5—5.75 (4 H, CH=C). ^{13}C NMR ($CDCl_3$), δ: 31.38 (C-5); 39.35; 40.10 (CH_2 in the allyl group); 46.20; 51.45 (C-2, C-6); 116.97; 117.22 (=CH_2 in the allyl group); 124.65; 129.24 (C-3,C-4); 134.84; 135.12 (=CH— in the allyl group).

Scheme 8



Hydrochloride 2 · HCl was obtained from compound **2** (2.08 g, 10.4 mmol) and ethereal HCl, yield 2.37 g (93 %), m.p. 177.5—178.5 °C (from an ether—methanol mixture). Found (%): C, 66.13; H, 9.14; N, 7.26; Cl, 17.88. $C_{11}H_{18}NCl$. Calculated (%): C, 66.15; H, 9.08; N, 7.01; Cl, 17.75. IR (CH_2Cl_2), ν/cm^{-1}: 1439, 1472, 1647, 3090 (CH=CH_2 and CH=CH); 1585 (NH_2^+). ^1H NMR ($CDCl_3$), δ: 2.15—2.52 (4 H, CH_2—C=); 2.8—2.95 (2 H, CH_2—C=); 3.40 (m, 1 H, H-6); 3.85 (br.s, 1 H, H-2); 5.15—5.53 (4 H, CH_2=C); 5.6—5.85 (4 H, CH=); 9.7 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 26.07 (C-5); 35.50; 36.88 (CH_2 in the allyl group); 49.16; 50.40 (C-2, C-6); 119.42; 119.80 (=CH_2 in the allyl group); 123.23; 124.81 (C-3, C-4); 131.48; 131.78 (=CH— in the allyl group).

***N*-Benzyl-*trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine (17).** A mixture of compound **2** (3.35 g, 20.5 mmol), benzyl chloride (2.36 mL, 20.5 mmol), K_2CO_3 (5.67 g, 41 mmol), and ethanol (10 mL) was boiled for 5 h, then the EtOH was distilled off *in vacuo*, and water was added until the K_2CO_3 dissolved completely. The mixture was extracted with ether, and the extract was dried with K_2CO_3. Distillation gave 4.66 g (92 %) of compound **18**, b.p. 140—142 °C (2 Torr). The product obtained was passed through a column with SiO_2 (pentane as the eluent) and distilled; b.p. 140—141 °C (2 Torr), n_D^{25} 1.5322. Found (%): C, 85.42; H, 9.22; N, 5.62. $C_{18}H_{23}N$. Calculated (%): C, 85.32; H, 9.15; N, 5.53. MS (EI, 70 eV), *m/z*: 212 $[M-C_3H_5]^+$. IR (pure compound, ν/cm^{-1}): 1435, 1450, 1490, 1640, 3080 (CH=CH_2 and CH=CH). ^1H NMR ($CDCl_3$), δ: 1.9 (m, 2 H, H-5); 2.06—2.47 (4 H, CH_2—C=); 3.02 (m, 2 H, H-2, H-6); 3.60 (AB-spectrum; δ_A 3.50; δ_B 3.70; J_{AB} = 13.73 Hz; 2 H; CH_2Ph); 4.86—5.12 (m, 4 H, CH_2=C); 5.5—5.96 (4 H, CH=C); 7.1—7.45 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 26.61 (C-5); 35.19; 38.53 (CH_2 in the allyl group); 50.34; 51.50 (C-2, C-6); 56.69 (N—C—Ph); 115.42; 115.54 (CH_2 in the allyl group); 124.97; 126.42 (C-3, C-4); 127.85; 128.57; 128.98; 140.42 (Ph); 136.21; 136.72 (=CH— in the allyl group).

***N,N*-Dimethyl-*trans*-2,6-diallyl-1,2,5,6-tetrahydropyridinium iodide (15).** A mixture of compound **2** (0.74 g, 4.5 mmol), MeI (0.6 mL, 9 mmol), K_2CO_3 (1.25 g, 9 mmol), and EtOH (10 mL) was boiled for 5 h and filtered, and then the EtOH was evaporated to dryness *in vacuo*. The residue was extracted with chloroform and filtered once more, and the $CHCl_3$ was evaporated *in vacuo*. Recrystallization from an ethyl acetate — EtOH mixture gave 1.11 g (77 %) of product **15**, m.p. 145—146 °C. Found (%): C, 49.01; H, 7.01; N, 4.28; I, 39.61. $C_{13}H_{22}NI$. Calculated (%): C, 48.91; H, 6.95; N, 4.39; I, 39.75. MS (EI, 70 eV), *m/z*: 278 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}): 1415, 1438, 1481, 1644, 3042 (CH=CH_2 and CH=CH). ^1H NMR ($CDCl_3$), δ: 2.28—2.6 (4 H, CH_2); 2.93—3.12 (m, 2 H, CH_2); 3.38 (s, 3 H, CH_3); 3.51 (s, 3 H, CH_3); 4.15 (m, 1 H, H-6); 4.51 (br.d, 1 H, H-2); 5.17—5.42 (4 H, CH_2=C); 5.69—6.08 (4 H, CH=H). ^{13}C NMR ($CDCl_3$), δ: 25.33 (C-5); 31.87; 33.15 (CH_2 in the allyl group); 47.67; 48.59 (N^+—CH_3); 65.63; 66.47 (C-2, C-6); 119.44; 119.77 (=CH_2 in the allyl group); 122.15; 123.10 (C-3, C-4); 130.58; 130.89 (=CH— in the allyl group).

***trans*-2,6-Diallyl-5-deutero-1,2,5,6-tetrahydropyridine (3).** Pyridine (5.7 mL, 70 mmol) and then CH_3OD (5.9 mL,

140 mmol) were added at −70 °C to a solution of triallylborane (4.65 g, 35 mmol) in ether (20 mL). The reaction mixture was refluxed for 4 h (46 °C). Distillation gave 4.52 g (78 %) of compound **3**, b.p. 68 °C (2 Torr), $n_D^{22.5}$ 1.4868. Found (%): C, 80.15; H, 9.71; D, 1.32; N, 8.60. $C_{11}H_{16}DN$. Calculated (%): C, 80.43; H, 9.82; D, 1.23; N, 8.53. MS (EI, 70 eV), *m/z*: 123 $[M-C_3H_5]^+$. IR (pure compound, ν/cm^{-1}): 1439, 1461, 1641, 3030, 3079 (—CH=CH_2 and CH=CH); 3330 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.66 (m, 1 H, NH); 1.8—2.17 (5 H, CH_2+CHD); 2.75 (m, 1 H, H-6); 3.22 (m, 1 H, H-2); 4.80—5.0 (4 H, CH_2=C); 5.4—5.72 (4 H, CH=C). ^{13}C NMR ($CDCl_3$), δ: 31.22 (C-5); 39.22; 39.90 (CH_2 in the allyl group); 45.99; 51.29 (C-2, C-6); 116.83; 117.08 (=CH_2 in the allyl group); 124.46; 129.15 (C-3, C-4); 134.99; 135.30 (=CH— in the allyl group).

Hydrochloride 3 • HCl was obtained from compound **3** (1.21 g, 7.3 mmol) and an ethereal solution of HCl, yield 1.45 g (98 %), m.p. 169.5—170 °C (from an ether—methanol mixture). Found (%): C, 65.56; H, 8.35; D, 1.08; N, 6.61; Cl, 17.69. $C_{11}H_{17}DNCl$. Calculated (%): C, 65.82; H, 8.54; D, 1.00; N, 6.98; I, 17.66. IR (CH_2Cl_2, ν/cm^{-1}): 1436, 1470, 1644, 3048 (CH=CH_2 and CH=CH); 1584 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 2.23—2.65 (3 H, CH_2+CHD); 2.84—3.07 (2 H, CH_2); 3.5 (m, 1 H, H-6); 3.91 (m, 1 H, H-2); 5.1—5.37 (4 H, CH_2=C); 5.68—5.98 (4 H, CH=C); 9.56 br.s and 10.02 br.s (2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 25.55 (C-5); 35.33; 36.72 (CH_2 in the allyl group); 48.93; 50.23 (C-2, C-6); 119.30; 119.68 (=CH_2 in the allyl group); 123.10; 124.60 (C-3, C-4); 131.35; 131.65 (=CH— in the allyl group).

***N*-Benzyl-*trans*-2,6-diallyl-5-deutero-1,2,5,6-tetrahydropyridine (19).** A mixture of compound **3** (1.55 g, 9 mmol), benzyl chloride (1.1 mL, 9 mmol), K_2CO_3 (2.6 g, 18 mmol), and ethanol (5 mL) was refluxed for 5 h, then the EtOH was distilled off *in vacuo*. Water was added until the K_2CO_3 dissolved completely, and the solution was extracted with ether. The ethereal extract was dried with K_2CO_3. Distillation gave 1.95 g (82 %) of compound **20**, b.p. 113—114 °C (1 Torr). B.p. after the second distillation was 114 °C (1 Torr), n_D^{21} 1.5348. Found (%): C, 84.70; H, 8.69; D, 0.61; N, 5.60. $C_{18}H_{22}DN$. Calculated (%): C, 84.99; H, 8.72; D, 0.79; N, 5.51. IR (CH_2Cl_2), ν/cm^{-1}: 1455, 1497, 1641, 3030, 3081 (CH=CH_2 and CH=CH). ^{1}H NMR ($CDCl_3$) δ: 1.86 (m, 1 H, H-5); 2.0—2.43 (4 H, CH_2—C=); 2.98 (m, 2 H, H-2 and H-6); 3.55 (AB-spectrum; δ_A 3.43; δ_B 3.67; J_{AB} = 13.85 Hz; 2 H; CH_2Ph); 4.84—5.08 (4 H, CH_2=C); 5.5—5.92 (4 H, CH=C); 7.06—7.4 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 26.16 (C-5); 35.14; 38.46 (CH_2 in the allyl group); 50.29; 51.31 (C-2, C-6); 56.58 (N—C—Ph); 115.36; 115.49 (=CH_2 in the allyl group); 124.81; 128.97 (C-3, C-4); 126.37; 127.77; 128.48; 140.27 (Ph); 136.07; 136.59 (=CH— in the allyl group).

***trans*-2,6-Dipropylpiperidine (5).** A mixture of compound **2** (10.77 g, 66 mmol), acetic acid (50 mL), and Raney nickel (0.2 g) was placed in an autoclave (0.5 L), then H_2 was fed up to 95 atm pressure, and the mixture was heated for 10 h at 95—100 °C. The nickel was separated, then 20 % NaOH was added until the acetic acid was completely neutralized (pH > 7). The mixture was extracted with ether, and the extract was dried with K_2CO_3. Distillation gave 9.52 g (85 %) of compound **5**, b.p. 64—65 °C (2 Torr). The compound obtained after repeated distillation had b.p. 57—58 °C (1 Torr), $n_D^{22.5}$ 1.4541. Found (%): C, 78.12; H, 13.51; N, 8.31. $C_{11}H_{23}N$. Calculated (%): C, 78.03; H, 13.69; N, 8.27. MS (EI, 70 eV), *m/z*: 169 $[M]^+$. IR (pure compound), ν/cm^{-1}: 3270 (NH). ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, *J* = 6.51 Hz; 6 H, CH_3); 1.15—1.70 (15 H; CH_2+NH); 2.83 (m, 2 H, H-6+H-2). ^{13}C NMR ($CDCl_3$), δ: 13.68 (CH_3 in Pr); 18.64; 19.01; 19.35 (C-3, C-4, C-5); 30.82; 36.20 (CH_2 in Pr); 49.85 (C-2, C-6).

Hydrochloride 5 • HCl was obtained from compound **5** (1.20 g, 5.83 mmol) and an ethereal solution of HCl, yield 1.29 g (88 %), m.p. 302 °C (from an ether—methanol mixture). Found (%): C, 64.45; H, 11.67; N, 6.76; Cl, 17.36. $C_{11}H_{24}NCl$. Calculated (%): C, 64.20; H, 11.75; N, 6.81; Cl, 17.23. IR ($CHCl_3$), ν/cm^{-1}: 1590 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.00 (t, *J* = 6.43 Hz; 6 H, CH_3); 1.40 (m, 4 H, CH_2), 1.7 (m, 6 H, CH_2); 2.00 (m, 4 H, CH_2); 3.32 (br.s, 2 H, H-6+H-2), 9.3 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 13.34 (CH_3 in Pr); 16.91 (C-4); 18.61 (C-3, C-5); 25.57; 32.03 (CH_2 in Pr); 51.56 (C-2, C-6).

***N*-Benzyl-*trans*-2,6-dipropylpiperidine (7)** was obtained similarly to compound **17** from compound **5** (3.36 g, 19.8 mmol). Yield 4.34 g (84 %), b.p. 120—121 °C (1 Torr), n_D^{20} 1.5162. Found (%): C, 83.21; H, 11.13; N, 5.28. $C_{18}H_{29}N$. Calculated (%): C, 83.33; H, 11.27; N, 5.39. MS (EI, 70 eV), *m/z*: 216 $[M-C_3H_7]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1030, 1110, 1138, 1205, 1495, 1602, 3030, 3090. ^{1}H NMR ($CDCl_3$), δ: 0.83 (t, *J* = 6.71 Hz, 6 H, CH_3); 1.12—1.45 (m, 8 H, CH_2—); 1.45—1.72 (m, 6 H, CH_2); 2.75 (br.s, 2 H, H-2, H-6); 3.66 (AB-spectrum; δ_A 3.60; δ_B 3.70; J_{AB} = 14.04 Hz; 2 H, CH_2Ph); 7.03—7.48 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 14.25 (CH_3 in Pr); 19.65; 20.77 (C-3, C-4, C-5); 24.74; 34.29 (CH_2 in Pr); 49.40 (C-2, C-6); 53.38 (N—C—Ph); 126.23; 127.87; 128.34; 141.62 (Ph).

***N,N*-Dimethyl-*trans*-2,6-dipropyl-1,2,5,6-tetrahydropiperidinium iodide (6)** was obtained similarly to **15** from **5** (0.14 g, 0.8 mmol) in 0.19 g (70 %) yield, m.p. 225.5—226.5 °C (from an ethyl acetate — ethanol mixture). Found (%): C, 47.98; H, 8.64; N, 4.22; I, 39.02. $C_{13}H_{28}NI$. Calculated (%): C, 48.00; H, 8.68; N, 4.31; I, 39.01. MS (EI, 70 eV), *m/z*: 282 $[M-C_3H_7]^+$. IR (KBr pellets), ν/cm^{-1}: 1417, 1479, 2879, 2962. ^{1}H NMR ($CDCl_3$), δ: 0.96—1.09 (t, 6 H, CH_3); 1.35—2.2 (14 H, CH_2); 3.37 (s, 6 H, CH_3); 3.64—3.8 (m, 2 H, H-2, H-6). ^{13}C NMR ($CDCl_3$), δ: 13.82 (CH_3 in Pr); 16.24 (C-4); 19.79 (C-3, C-5); 23.52; 29.13 (CH_2 in Pr); 49.02 (N^+—CH_3); 70.08 (C-2, C-6).

***cis*-2,6-Diallyl-1,2,5,6-tetrahydropyridine (4).** *trans*-2,6-Diallyl-1,2,5,6-tetrahydropyridine **2** (21.66 g, 133 mmol) was placed in a three-neck flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an argon inlet, then triallylborane (24 mL, 137 mmol) was added. This was accompanied by insignificant self-heating. The mixture was heated at 125—130 °C for 5 h, then methanol (5 mL) and 20 % NaOH (40 mL) were successively added at 0 °C. The mixture was extracted with ether, and the extract was dried with K_2CO_3. Distillation gave 19.26 g (89 %) of compound **4**, b.p. 51—54 °C (1 Torr). An admixture of the *trans*-isomer (2—3 %) was separated on a column with SiO_2 using pentane as the eluent. The pure compound **4** had b.p. 52—53 °C (1 Torr), n_D^{21} 1.4858. Found (%): C, 80.85; H, 10.43; N, 8.60. $C_{11}H_{17}N$. Calculated (%): C, 80.92; H, 10.49; N, 8.58. MS (EI, 70 eV), *m/z*: 122 $[M-C_3H_5]^+$. IR ($CHCl_3$), ν/cm^{-1}: 1642, 1840, 3008, 3082 (CH_2=CH, CH=CH); 3310 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.65 (br.s, 1 H; NH); 1.75—2.03 (2 H, CH_2—C=); 2.05—2.35 (4 H, CH_2—C=); 2.82 (m, 1 H, H-6); 3.4 (m, 1 H, H-2); 5.0—5.2 (4 H, CH_2=C); 5.53—5.9 (4 H, CH=C). ^{13}C NMR ($CDCl_3$), δ: 31.80 (C-5); 40.16; 40.48 (CH_2 in the allyl group); 51.70; 53.77 (C-2, C-6); 116.80 (CH_2= in the allyl group); 124.91; 129.56 (C-3, C-4); 134.48 (CH= in the allyl group).

Hydrochloride 4 • HCl was obtained in 84 % yield, m.p. 225—226 °C (from an ether—methanol mixture). Found (%):

C, 66.09; H, 9.12; N, 7.23; Cl, 17.57. $C_{11}H_{18}NCl$. Calculated (%): C, 66.15; H, 9.08; N, 7.01; Cl, 17.75. IR (KBr pellets, ν/cm^{-1}: 1430, 1462, 1641, 3078 (CH=CH_2 and CH=CH); 1580, sh 1598 (NH_2^+). ^1H NMR ($CDCl_3$), δ: 2.20—2.80; 2.95—3.3 (7 H, CH_2—C= + H-6); 3.90 (br.s, 1 H, H-2); 5.15 (m, 4 H, CH_2=C); 5.65—6.0 (4 H, CH=C); 9.5 br.s and 10.1 br.s (2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 27.90 (C-5); 36.74; 37.28 (CH_2 in the allyl group); 54.33; 54.68 (C-2, C-6); 119.37; 119.80 (=CH_2 in the allyl group); 123.36; 125.77 (C-3, C-4); 131.64; 131.72 (=CH— in the allyl group).

***N*-Benzyl-*cis*-2,6-diallyl-1,2,5,6-tetrahydropyridine (18)** was obtained similarly to compound **17** from **4** (1.02 g, 6 mmol), yield 0.94 g (62 %), b.p. 148—150 °C (2 Torr). Chromatography on SiO_2 (an ether—hexane mixture, 1 : 1, as the eluent) and a second distillation gave the compound with b.p. 150 °C (2 Torr), n_D^{20} 1.5395. Found (%): C, 85.19; H, 9.31; N, 5.48. $C_{18}H_{23}N$. Calculated (%): C, 85.32; H, 9.15; N, 5.53. MS (EI, 70 eV), *m/z*: 212 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1453, 1495, 1605, 1641, 3035, 3086 (CH_2=CH and CH=CH). ^1H NMR ($CDCl_3$), δ: 1.88—2.56 (6 H, CH_2); 2.96 (m, 1 H, H-6); 3.28 (m, 1 H, H-2); 3.90 (s, 2 H, CH_2—Ph); 4.98—5.1 (4 H, CH_2); 5.7—5.94 (4 H, CH); 7.26—7.52 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 26.54 (C-5); 38.80; 39.57 (CH_2 in the allyl group); 56.12; 59.19 (C-2, C-6); 56.66 (N—C—Ph); 116.03; 116.15 (=CH_2 in the allyl group); 123.57; 126.48 (C-3, C-4); 128.02; 128.14; 128.57; 141.18 (Ph); 136.53; 136.97 (=CH— in the allyl group).

***N,N*-Dimethyl-*cis*-2,6-diallyl-1,2,5,6-tetrahydropyridinium iodide (16)** was obtained similarly to compound **15** from **4** (2.63 g, 16 mmol), yield 4.57 g (89 %), m.p. 100—101 °C. Found (%): C, 49.02; H, 6.90; N, 4.38; I, 39.67. $C_{13}H_{22}NI$. Calculated (%): C, 48.91; H, 6.95; N, 4.39; I, 39.75. MS (EI, 70 eV), *m/z*: 278 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1412, 1480, 1644, 3040 (CH_2=CH and CH=CH). ^1H NMR ($CDCl_3$), δ: 2.2—2.66 (4 H, CH_2); 2.94 (s, 3 H, CH_3); 3.0—3.15 (m, 2 H, CH_2); 3.58 (s, 3 H, CH_3); 4.35 (m, 1 H, H-6); 4.81 (br.d, 1 H, H-2); 5.15—5.44 (4 H, CH_2=C); 5.64 (d, 1 H, CH=); 5.73—6.09 (3 H, CH=). ^{13}C NMR ($CDCl_3$), δ: 26.64 (C-5); 32.40; 32.62 (CH_2 in the allyl group); 38.93; 48.72 (N^+—CH_3); 68.74; 69.45 (C-2, C-6); 119.67; 120.05 (=CH_2 in the allyl group); 121.67; 124.96 (C-3, C-4); 130.50 (=CH— in the allyl group).

***cis*-2,6-Dipropylpiperidine (8).** Similarly to the synthesis of compound **5**, hydrogenation of compound **4** (10.60 g, 64.9 mmol) in acetic acid (50 mL) in the presence of Raney nickel (0.2 g) at 95—100 °C and 95 atm of H_2 for 10 h gave 9.85 g (90 %) of product **8**, b.p. 58—64 °C (1 Torr). The compound after the second distillation had b.p. 62 °C (1 Torr), n_D^{20} 1.4531. Found (%): C, 78.24; H, 13.51; N, 8.35. $C_{11}H_{23}N$. Calculated (%): C, 78.03; H, 13.69; N, 8.27. MS (EI, 70 eV), *m/z*: 169 $[M]^+$. IR (pure compound), ν/cm^{-1}: 1100, 1128, 1311, 1330, 1379, 2800, 1440, 1452, 1462. ^1H NMR ($CDCl_3$), δ: 0.83—1.15 (m, 8 H; 2 CH_3 + CH_2); 1.25—1.45 (m, 10 H); 1.56—1.85 (m, 3 H); 2.45—2.55 (br.s, 2 H, H-6 and H-2). ^{13}C NMR ($CDCl_3$), δ: 13.99 (CH_3 in Pr); 18.89; 24.66 (C-3, C-4, C-5); 32.51; 39.47 (CH_2 in Pr); 56.60 (C-2, C-6).

Hydrochloride 8 · HCl was obtained in 89 % yield, m.p. 225—226 °C (from an ether—methanol mixture). Found (%): C, 64.32; H, 11.77; N, 6.97; Cl, 17.49. $C_{11}H_{24}NCl$. Calculated (%): C, 64.20; H, 11.75; N, 6.81; Cl, 17.23. IR (CH_2Cl_2), ν/cm^{-1}: 1590 (NH_2^+); 1115, 1386, 1468, 2968. ^1H NMR ($CDCl_3$), δ: 0.85 (t, 6 H, CH_3); 1.1—1.95 (m, 12 H); 2.0—2.22 (m, 2 H); 2.87 (m, 2 H, H-6 and H-2); 8.8—9.2 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 13.53 (CH_3 in Pr); 18.56; 22.62 (C-3, C-4, C-5); 27.45; 34.63 (CH_2 in Pr); 58.37 (C-2, C-6).

***N*-Benzyl-*cis*-2,6-dipropylpiperidine (13).** Similarly to the synthesis of compound **17**, compound **13** (3.64 g, 69 %; b.p. 118—120 °C/1 Torr) was obtained from compound **8** (3.44 g, 20.3 mmol). The compound after the second distillation had b.p. 120 °C (1 Torr), n_D^{20} 1.5132. Found (%): C, 83.51; H, 11.02; N, 5.45. $C_{18}H_{29}N$. Calculated (%): C, 83.33; H, 11.27; N, 5.39. MS (EI, 70 eV), *m/z*: 216 $[M-C_3H_7]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1029, 1100, 1454, 1465, 1494, 1602, 3030. ^1H NMR ($CDCl_3$), δ: 0.65—0.85 (m, 6 H, CH_3); 1.1—1.6 (m, 14 H, CH_2); 2.54 (m, 2 H, H-2 and H-6); 3.65 (s, 2 H, CH_2—Ph); 7.05—7.4 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 14.21 (CH_3 in Pr); 19.97; 23.72 (C-3, C-4, C-5); 27.64; 37.06 (CH_2 in Pr); 51.52 (N—C—Ph); 62.85 (C-2, C-6); 125.77; 127.54; 127.71; 143.48 (Ph).

***N,N*-Dimethyl-*cis*-2,6-dipropylpiperidinium iodide (14)** was obtained similarly to compound **15** from **8** (2.9 g, 17 mmol), yield 5.49 g (99 %), m.p. 142.5—143 °C. Found (%): C, 48.02; H, 8.85; N, 4.56; I, 38.91. $C_{13}H_{28}NI$. Calculated (%): C, 48.00; H, 8.68; N, 4.31; I, 39.01. MS (EI, 70 eV), *m/z*: 324 $[M-H]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1140, 1470, 2879, 2963, 3039. ^1H NMR ($CDCl_3$), δ: 1.0 (t, 6 H, CH_3 in Pr); 1.39—1.6 (6 H, CH_2); 1.7—1.93 (4 H, CH_2); 1.94—2.13 (4 H, CH_2); 2.88 (s, 3 H, N—CH_3); 3.4 (s, 3 H, N—CH_3); 3.95 (m, 2 H, H-2 and H-6). ^{13}C NMR ($CDCl_3$), δ: 13.12 (CH_3 in Pr); 19.36 (C-3, C-5); 20.65 (C-4); 25.61; 31.06 (CH_2 in Pr); 37.24; 48.69 (N^+—CH_3); 73.12 (C-2, C-6).

***trans*-2,6-Diallyl-2,3,4,5,6-pentadeutero-1,2,5,6-tetrahydropyridine (21).** A mixture of triallylborane (3.13 g, 23 mmol), deuteropyridine (3.9 mL, 46 mmol), methanol (3.7 mL, 92 mmol), and ether (20 mL) was refluxed for 4 h at 42 °C. The low-boiling compounds were distilled off *in vacuo*, then triethanolamine (3 mL, 23 mmol) was added to the residue. Distillation gave 2.87 g (74 %) of compound **21**, b.p. 64—64.5 °C (2 Torr), n_D^{20} 1.4869. Found (%): C, 78.53; H, 7.21; D, 6.02; N, 8.44. $C_{11}H_{12}D_5N$. Calculated (%): C, 78.51; H, 7.19; D, 5.98; N, 8.32. MS (EI, 70 eV), *m/z*: 127 $[M-C_3H_5]^+$. IR ($CHCl_3$), ν/cm^{-1}: 1442, 1641, 3079 (CH=CH_2 and CH=CH); 3330 (NH). ^1H NMR ($CDCl_3$), δ: 1.83 (br.s, 2 H, H-5 + NH); 1.98—2.34 (4 H, CH_2); 4.98—5.2 (4 H, 2 CH_2=); 5.63—5.88 (2 H, 2 CH=). ^{13}C NMR ($CDCl_3$), δ: 30.61 (C-5); 39.23; 39.91 (CH_2 in the allyl group); 45.64; 50.82 (C-2,C-6); 116.80; 117.04 (=CH_2 in the allyl group); 124.11 (C-4); 128.71 (C-3); 135.13; 135.35 (=CH— in the allyl group).

Hydrochloride 21 · HCl was obtained in 92 % yield, m.p. 170.5—171 °C (from an ether—methanol mixture). Found (%): C, 64.53; H, 6.62; D, 5.08; N, 7.01; Cl, 17.53. $C_{11}H_{13}D_5NCl$. Calculated (%): C, 64.53; H, 6.40; D, 4.92; N, 6.84; Cl, 17.31. IR (CH_2Cl_2), ν/cm^{-1}: 1453, 1643, 3046, (CH_2=CH and CH=CH), 1582 (NH_2^+). ^1H NMR ($CDCl_3$), δ: 2.28 (s, 1 H, H-5); 2.51 (m, 2 H, CH_2); 2.94 (m, 2 H, CH_2); 5.22 (m, 4 H, CH_2=C); 5.80 (m, 2 H, CH=C); 9.6 br.s and 10.08 br.s (2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 25.46 (C-5); 35.39, 36.75 (CH_2 in the allyl group); 48.70, 49.92 (C-2,C-6); 119.43, 119.81 (=CH_2 in the allyl group); 122.78, 124.39 (C-3, C-4); 131.44, 131.75 (=CH— in the allyl group).

***N*-Benzyl-2,6-diallyl-2,3,4,5,6-pentadeutero-1,2,5,6-tetrahydropyridine (23)** was obtained similarly to compound **17** from **21** (1 g, 5,9 mmol), yield 1.53 g (99 %), b.p. 120—121 °C (1 Torr), n_D^{21} 1.5344. Found (%): C, 83.85; H, 7.14; D, 3.86; N, 5.40; $C_{18}H_{18}D_5N$. Calculated (%): C, 83.66; H, 7.02; D, 3.90; N, 5.42. MS (EI, 70 eV), *m/z*: 217 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1456, 1496, 1640, 3030, 3081 (CH_2=CH and CH=CH). ^1H NMR ($CDCl_3$), δ: 1.85 (s, 1 H, H-5); 2.05—2.42 (4 H, CH_2—C=); 3.6 (AB-spectrum, δ_A 3.43; δ_B 3.68; J_{AB} = 13.73 Hz; 2 H, CH_2Ph); 4.85—5.1

(4 H, CH_2=C); 5.58—5.95 (2 H, CH=C); 7.08—7.39 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 25.88 (C-5); 35.30; 38.46 (CH_2 in the allyl group); 50.20 (N—C—Ph); 50.92; 56.09 (C-2, C-6); 115.41; 115.53 (=CH_2 in the allyl group); 124.54; 127.84 (C-3, C-4); 126.42; 128.56; 140.41 (Ph); 136.20; 136.68 (=CH— in the allyl group).

***trans*-2,6-Diallyl-2,3,4,5,5,6-hexadeutero-1,2,5,6-tetrahydropyridine (22).** A mixture of deuteropyridine (5.39 g, 64.2 mmol), triallylborane (11.2 mL, 64.2 mmol), and CH_3OD (10.73 mL, 257 mmol) was refluxed for 5 h, treated with 20 % NaOH (19 mL), and extracted with ether; the extract was dried with K_2CO_3. Distillation gave 6.81 g (63 %) of compound **22**, b.p. 42—43 °C (1 Torr), n_D^{20} 1.4870. Found (%): C, 78.10; H, 6.73; D, 7.32; N, 8.50. $C_{11}H_{11}D_6N$. Calculated (%): C, 78.04; H, 6.55; D, 7.14; N, 8.27. MS (EI, 70 eV), *m/z*: 128 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1441, 1640, 1628 sh, 3006, 3041, 3082 (CH=CH and CH=CH_2), 3323 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.70 (s, 1 H, NH); 2.0—2.28 (4 H, CH_2—); 4.95—5.14 (4 H, CH_2=C); 5.6—5.87 (2 H, CH=C). ^{13}C NMR ($CDCl_3$), δ: 29.43 (C-5); 38.49, 39.13 (CH_2 in the allyl group); 44.78, 49.98 (C-2, C-6); 115.91, 116.13 (=CH_2 in the allyl group); 123.19, 128.07 (C-3, C-4); 134.30, 134.62 (=CH— in the allyl group).

Hydrochloride 22 · HCl was obtained in 87 % yield, m.p. 170.5—171.5 °C (from an ether—methanol mixture). Found (%): C, 64.30; H, 5.96; D, 5.71; N, 7.02; Cl, 17.28. $C_{11}H_{12}D_6NCl$. Calculated (%): C, 64.21; H, 5.88; D, 5.87; N, 6.81; Cl, 17.23. IR (CH_2Cl_2), ν/cm^{-1}: 1646, 3025 (CH=CH and CH=CH_2), 1585 (NH_2^+). ^{1}H NMR ($CDCl_3$), δ: 2.50 (td, J = 8.21 Hz, J = 7.95 Hz, 2 H, CH_2—); 2.95 (m, 2 H, CH_2—); 5.22 (m, 4 H, CH_2=C); 5.85 (m, 2 H, CH=C); 9.58 br.s and 10.02 br.s (2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 25.03 (C-5); 35.27, 36.69 (CH_2 in the allyl group); 48.58, 49.85 (C-2, C-6); 119.36, 119.74 (=CH_2 in the allyl group); 122.79, 124.25 (C-3, C-4); 131.40, 131.71 (=CH— in the allyl group).

***N*-Benzyl-2,6-diallyl-2,3,4,5,5,6-hexadeutero-1,2,5,6-tetrahydropyridine (24)** was obtained similarly to compound **17** from **23** (3.59 g, 21 mmol), yield 3.84 g (70 %), b.p. 115 °C (1 Torr), n_D^{20} 1.5347. Found (%): C, 83.47; H, 6.85; D, 4.83; N, 5.26. $C_{18}H_{17}D_6N$. Calculated (%): C, 83.34; H, 6.60; D, 4.66; N, 5.40. MS (EI, 70 eV), *m/z*: 218 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1606, 1641, 3004, 3030, 3080 (CH=CH and CH=CH_2). ^{1}H NMR ($CDCl_3$), δ: 1.98—2.43 (4 H, CH_2—); 3.53 (AB-spectrum, δ_A 3.41, δ_B 3.65, J_{AB} = 13.73 Hz, 2 H, CH_2—Ph); 4.8—5.1 (4 H, CH_2=C); 5.54—5.94 (2 H, CH=C); 7.02—7.4 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 25.39 (C-5); 35.04, 38.33 (CH_2 in the allyl group); 50.10 (N—C—Ph); 50.68, 55.93 (C-2, C-6); 115.27, 115.39 (=CH_2 in the allyl group); 124.29, 127.70 (C-3, C-4); 135.98, 136.48 (=CH— in the allyl group); 126.31, 128.40, 140.16 (Ph).

***trans*-2,6-Diallyl-3-bromo-1,2,5,6-tetrahydropyridine (25).** 3-Bromopyridine (13.8 mL, 143.1 mmol) and then methanol (15.5 mL, 382 mmol) were added with cooling (−70 °C) to triallylborane (12.79 g, 95.4 mmol). The reaction mixture was refluxed for 6 h, treated with 20 % NaOH (30 mL), and extracted with ether. The extract was dried with K_2CO_3. Distillation gave 16.75 g (72 %) of compound **25**, b.p. 80—85 °C (1 Torr). Additional distillation gave the compound with b.p. 85—86 °C (1 Torr), n_D^{20} 1.5251. Found (%): C, 54.41; H, 6.76; N, 5.83; Br, 33.36. $C_{11}H_{16}NBr$. Calculated (%): C, 54.55; H, 6.66; N, 5.78; Br, 33.00. MS (EI, 70 eV), *m/z*: 201 $[M-C_3H_5]^+$. IR (pure compound, ν/cm^{-1}: 1435, 1452, 1640, 3079 (CH_2=CH and CH=CH); 3318 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.78—2.4 (6 H, CH_2—C=); 2.6 (m, 1 H, NH); 2.94 (m, 1 H, H-6); 3.41 (d, 1 H, H-2); 5.0—5.18 (4 H, CH_2=C); 5.63—5.9 (2 H, CH=C); 6.0—6.1 (1 H, H-4). ^{13}C NMR ($CDCl_3$), δ: 34.09 (C-5); 36.16; 39.66 (CH_2 in the allyl group); 44.91; 58.11 (C-2, C-6); 117.09; 117.69 (=CH_2 in the allyl group); 124.34 (C-3); 127.34 (C-4); 134.55; 134.92 (=CH— in the allyl group).

Hydrochloride 25 · HCl was obtained in 83 % yield, m.p. 165—166 °C (from an ether—methanol mixture). Found (%): C, 47.47; H, 6.29; N, 5.03; Br, 28.47; Cl, 12.51. $C_{11}H_{17}NBrCl$. Calculated (%): C, 47.41; H, 6.15; N, 5.03; Br, 28.68; Cl, 12.72. IR ($CHCl_3$), ν/cm^{-1}: 1434, 1648 (CH_2=CH and CH=CH); 1580 (NH_2^+). ^{1}H NMR ($CDCl_3$), δ: 2.35—2.6 (3 H, CH_2—C=); 2.8—3.18 (3 H, CH_2—C=); 3.55 (br.s, 1 H, H-6); 4.1 (s, 1 H, H-2); 5.12—5.53 (4 H, CH_2=C); 5.64—6.1 (2 H, CH=C); 6.25 (m, 1 H, H-4); 9.7 and 10.6 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 29.15; 34.84; 35.88 (C-5, CH_2 in the allyl group); 49.27; 55.93 (C-2, C-6); 116.24 (C-3); 120.03; 121.35 (=CH_2 in the allyl group); 128.29 (C-4); 131.18; 131.40 (=CH— in the allyl group).

***trans*-2,6-Diallyl-*N*-benzyl-3-bromo-1,2,5,6-tetrahydropyridine (27)** was obtained similarly to compound **17** from **25** (9.96 g, 41 mmol), yield 8.17 g (60 %), b.p. 150—154 °C (1.5 Torr). Chromatography on SiO_2 (an ether—pentane mixture, 3 : 1 as the eluent) followed by a second distillation gave the compound with b.p. 148 °C (1 Torr), $n_D^{20.5}$ 1.5551. Found (%): C, 65.01; H, 6.72; N, 4.24; Br, 24.32. $C_{18}H_{22}NBr$. Calculated (%): C, 65.06; H, 6.67; N, 4.22; Br, 24.05. MS (EI, 70 eV), *m/z*: 291 $[M-C_3H_5]^+$. IR (pure compound, ν/cm^{-1}: 1439, 1452, 1495, 1500, 1640, 3029, 3079 (CH_2=CH and CH=CH). ^{1}H NMR ($CDCl_3$), δ: 2.02—2.71 (6 H, CH_2—CH=); 3.1—3.4 (2 H, H-2, H-6); 3.7 (AB-spectrum, δ_A 3.48; δ_B 3.93; J_{AB} = 13.70 Hz; 2 H, CH_2Ph); 4.95—5.3 (4 H, CH_2=C); 5.74 (m, 1 H, CH=C); 6.01 (m, 1 H, CH=C); 6.25 (br.s, 1 H, H-4); 7.23—4.47 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 30.10 (C-5); 35.66; 36.97 (CH_2 in the allyl group); 49.19 (N—C—Ph); 49.66; 63.93 (C-2, C-6); 126.01 (C-3); 126.80; 127.62; 127.95; 129.04; 139.38 (Ph, C-4); 136.06 (=CH— in the allyl group).

***cis*-2,6-Diallyl-3-bromo-1,2,5,6-tetrahydropyridine (28).** Compound **25** (8.67 g, 35.8 mmol) was added at 20 °C to triallylborane (4.80 g, 35.8 mmol). Weak self-heating was observed. The mixture was heated at 125—130 °C for 3 h, then MeOH (1 mL) and 20 % NaOH (11 mL, 54 mmol) were added successively. The reaction mixture was extracted with ether, and the extract was dried with K_2CO_3. Distillation gave 6.46 g (75 %) of *cis*-isomer **28**, b.p. 104 °C (2 Torr). The admixture of the *trans*-isomer (6 %) was separated by chromatography on SiO_2 using pentane as the eluent. Pure compound **28** had b.p. 98 °C (1.5 Torr), n_D^{20} 1.5242. Found (%): C, 54.50; H, 6.82; N, 5.70; Br, 33.37. $C_{11}H_{16}NBr$. Calculated (%): C, 54.55; H, 6.66; N, 5.78; Br, 33.00. MS (EI, 70 eV), *m/z*: 201 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1440, 1450, 1460, 1641, 3005, 3042, 3081 (CH_2=CH and CH=CH); 3324, sh 3294 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.8—2.25 (5 H, CH_2+NH); 2.35—2.6 (2 H, CH_2); 2.85 (m, 1 H, H-6); 3.58 (m, 1 H, H-2); 4.97—5.24 (4 H, CH_2=C); 5.63—5.88 (2 H, CH=C); 6.15 (m, 1 H, H-4). ^{13}C NMR ($CDCl_3$), δ: 34.63; 38.13; 40.00 (C-5, CH_2 in the allyl group); 51.24; 58.08 (C-2,C-6); 117.32; 118.43 (=CH_2 in the allyl group); 125.65 (C-3); 129.13 (C-4); 133.47; 134.30 (=CH— in the allyl group).

Hydrochloride 28 · HCl was obtained in 80 % yield, m.p. 162—162.5 °C (from an ether—methanol mixture). Found (%): C, 47.54; H, 6.00; N, 4.96; Br, 28.83; Cl, 12.79. $C_{11}H_{17}NBrCl$. Calculated (%): C, 47.41; H, 6.15; N, 5.03; Br, 28.68; Cl, 12.72. IR (KBr pellets, ν/cm^{-1}: 1430, 1642, 3038, 3080 (CH_2=CH and CH=CH); 1578, sh 1594 (NH_2^+). ^{1}H NMR

($CDCl_3$), δ: 2.5—3.2 (6 H, CH_2); 3.3 (br.s, 1 H, H-6); 4.15 (br.s, 1 H, H-2); 5.1—5.46 (4 H, CH_2=C); 5.72 (m, 1 H, H-4); 6.04—6.37 (2 H, CH=C); 9.35 and 10.3 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 29.26; 35.78; 36.20 (C-5, CH_2 in the allyl group); 53.93; 58.38 (C-2, C-6); 119.84; 121.28 (=CH_2 in the allyl group); 124.82 (C-3); 129.25 (C-4); 130.84; 131.46 (=CH— in the allyl group).

***cis*-2,6-Diallyl-*N*-benzyl-3-bromo-1,2,5,6-tetrahydropyridine (30)** was obtained similarly to compound **17** from **28** (1.42 g, 5.9 mmol), yield 1.16 g (61 %), b.p. 130 °C (1 Torr), n_D^{20} 1.5562. Found (%): C, 64.91; H, 6.78; N, 4.33; Br, 23.89. $C_{18}H_{22}NBr$. Calculated (%): C, 65.06; H, 6.67; N, 4.22; Br, 24.05. MS (EI, 70 eV), *m/z*: 291 $[M-C_3H_5]^+$. IR (CH_2Cl_2), ν/cm^{-1}: 1454 (sh 1438), 1495, 1640, 3031, 3083 (CH_2=CH and CH=CH). ^1H NMR ($CDCl_3$), δ: 1.84—2.7 (6 H, CH_2—C=); 2.82 (m, 1 H, H-6); 3.2 (m, 1 H, H-2); 3.70 (AB-spectrum, δ_A 3.67; δ_B 3.77; J_{AB} = 13.93 Hz; 2 H, CH_2Ph); 4.86—5.09 (4 H, CH_2=C); 5.52—5.91 (2 H, CH=C); 6.07 (m, 1 H, H-4); 7.1—7.37 (5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 27.31; 37.61; 39.58 (C-5, CH_2 in the allyl group); 54.18 (N—C—Ph); 60.23; 64.38 (C-2, C-6); 115.85; 116.45 (=CH_2 in the allyl group); 124.68 (C-3); 126.07; 126.90; 128.00; 128.57; 139.56 (Ph); 136.58 (=CH— in the allyl group).

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