Transformations of pyridine and deuteropyridine under the action of trimethallylborane and alcohols. Synthesis of *trans*- and *cis*-2,6-dimethallyl-1,2,3,6-tetrahydropyridines and their *N*-derivatives*

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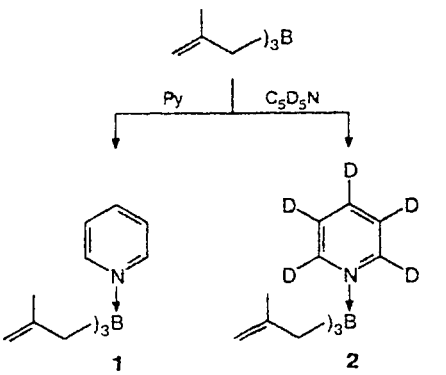
Reductive *trans*-2,6-dimethallylation of pyridine and deuteropyridine with trimethallylborane in the presence of alcohols proceeds at room temperature, *i.e.*, under substantially milder conditions than the analogous reaction with the participation of triallylborane. *trans*-2,6-Di(2-methylallyl)-1,2,3,6-tetrahydropyridine (**3**) was obtained in a yield of 87%. When heated with trimethallylborane (130—135 °C, 2.5 h), compound **3** underwent isomerization to *cis*-2,6-di(2-methylallyl)-1,2,3,6-tetrahydropyridine (**4**). Hydrogenation of *trans*- (**3**) and *cis*-isomers (**4**) yielded *trans*- and *cis*-2,6-diisobutylpiperidines, respectively. The heterocycles obtained were *N*-functionalized by reactions with MeI, $PhCH_2Cl$, ethylene oxide, and perfluoropropyloxirane. The stereochemistry of the *cis*- and *trans*-isomers (**3** and **4**) was established based on the NMR spectra of their *N,N*-dimethyl salts and the products of the reaction with ethylene oxide. *trans*-2,6-Dimethallyl-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridine and a number of its derivatives were prepared from the complex of trimethallylborane with C_5D_5N. A probable mechanism of the reductive *trans*-2,6-diallylation of pyridines with allylboranes in the presence of alcohols is discussed.

Key words: trimethallylborane, complexes with pyridine and deuteropyridine; pyridines, reductive *trans*-2,6-diallylation, *cis*- and *trans*-2,6-di(2-methylallyl)-1,2,3,6-tetrahydropyridines; *cis*- and *trans*-2,6-diisobutylpiperidines; oxiranes, *trans*→*cis* isomerization; β-aminoalcohols, stereochemistry.

Addition of nucleophilic reagents to pyridinium salts or adducts of pyridine with Lewis acids has long been known, and is the basis for various transformations of this class of heterocyclic compounds.[1—3]

Recently, it was demonstrated that when complexes of pyridine with triallyl-, tricrotyl-, and allyl(dialkyl)borane were treated with alcohols, water, or R_2NH, the aromatic system decomposed to form the corresponding *trans*-2,6-diallyl-Δ^3-piperideines in yields of up to 97%.[4—8] This new stereospecific reaction has a general character and is not complicated by side processes. This reaction was called **reductive *trans*-2,6-diallylation of pyridines with allylboranes**.[4,7] It was also found that when heated with triallyl- or allyl(dialkyl)boranes, *trans*-2,6-diallyl-Δ^3-piperideines are converted to the corresponding *cis*-isomers.[7—9] Therefore, both *trans*- and *cis*-2,6-diallyl-1,2,3,6-tetrahydropyridines and various of their derivatives can be prepared in virtually any desired amounts using only two key reagents, namely, triallylborane and pyridine (as well as 2-propanol and alkali).[7,8]

With the aim of extending the fields of application and searching for limitations of the reductive *trans*-α,α′-diallylation of aromatic nitrogen heterocycles with allyl derivatives of boron, we began to study reactions of this type involving trimethallylborane. The presence of one or two methallyl fragments in the molecule of the heterocycle allow one to carry out transformations that are impossible to perform with the use of the corre-



1 **2**

Compound	B.p./°C (*p*/Torr)	n_D^{20}	$\delta^{11}B$
1	75—77 (1)	1.5366	−0.5
2	81—82 (1.5)	1.5341	−0.7

* This article is dedicated to Prof. W. Siebert (Heidelberg) on the occasion of his 60th birthday.

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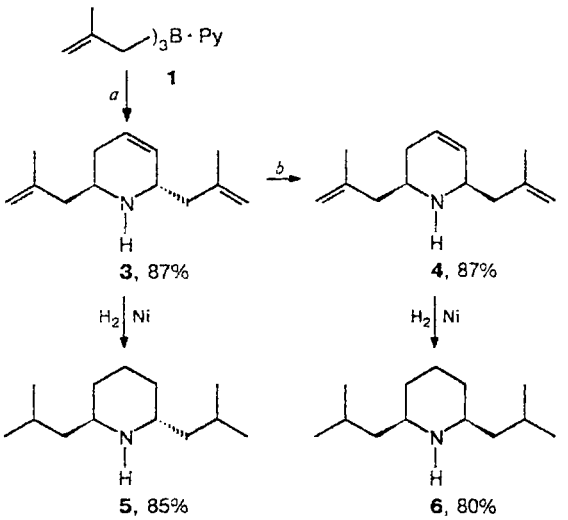
sponding allyl analogs, for example, oxidation to methylketones, ozonization, *etc.* In the course of these studies we also hope to obtain additional data on the reaction mechanism.

The reactions of trimethallylborane as Lewis acid with pyridine and deuteropyridine are accompanied by substantial heat evolution and yield adducts **1** and **2**, respectively. These adducts do not dissociate upon distillation *in vacuo* but oxidize readily in atmospheric oxygen.

The values of ^{11}B chemical shifts (δ −0.5 and −0.7 for **1** and **2**, respectively) unambiguously indicate that in these adducts the boron atom is tetrahedrally coordinated. (Other spectral characteristics of complexes **1** and **2** are given in the Experimental section.)

When treated with 2-propanol (4 equiv.), complex **1** was completely rearranged to *trans*-2,6-di(2-methylallyl)-1,2,3,6-tetrahydropyridine (**3**) (87%).



Reagents and conditions: *a*. 1) Pr^{i}OH, 20 °C, 2 h; 2) H_2O, OH^-; *b*. 1) Trimethallylborane, 130 °C; 2) MeOH; 3) H_2O, NaOH.

It should be noted that this reaction at room temperature was completed in 2 h, *i.e.*, it proceeded substantially more rapidly than that of the analogous complex with triallylborane (98 °C, 2—4 h).[4,5]

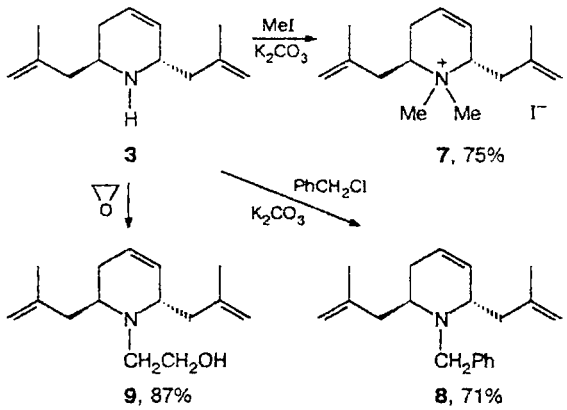
There is no need to use pure (distilled) complex **1** in the synthesis of amine **3**. The reaction is conveniently carried out as follows. Pyridine (2 equiv.) is added to trimethallylborane at 0—25 °C under an atmosphere of dry argon or nitrogen (exothermic reaction). Then 2-propanol (4 equiv.) is added, and the reaction mixture is stirred at 20 °C for 2 h. A 10% NaOH solution (1.2—1.5 equiv. of NaOH with respect to the initial trimethallylborane) is added, and the two-phase system is intensively stirred or boiled until boron completely disappeares in the organic phase (the green color of the flame). The resulting amine **3** is present in the organic layer. The second reaction product (methallylboric acid) reacts with NaOH to form the $[CH_2{=}C(CH_3)CH_2B(OH)_3]Na$ salt. The latter is transferred to the aqueous layer and partly hydrolyzed (isobutylene is evolved).

As expected,[7—9] when heated with trimethallylborane (1 : 1, 130—135 °C, 2.5 h), *trans*-amine **3** underwent virtually quantitative isomerization to the corresponding *cis*-compound **4**. *cis*-2,6-Di(2-methylallyl)-1,2,3,6-tetrahydropyridine (**4**) was isolated in the pure form by deboration of the aminoborane that formed followed by column chromatography on neutral Al_2O_3 (L 40/250, a 30 : 1 hexane—ether mixture as the eluent). The mechanism of *trans*→*cis* isomerization (**3**→**4**) is discussed below.

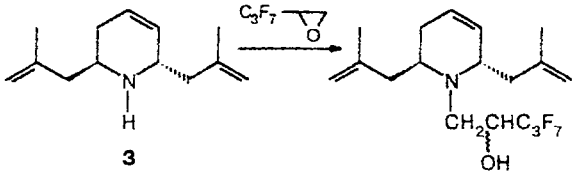
Hydrogenation of *trans*-isomer **3** over Raney nickel in acetic acid (100 atm. H_2, 95—100 °C, 13 h) gave *trans*-2,6-diisobutylpiperidine **5** (85%). Analogously, *cis*-2,6-diisobutylpiperidine **6** was obtained from *cis*-amine **4** in a yield of 80%.

Below are described chemical transformations of cyclic amines **3**—**6**, and the principal data that confirm their structures, including *cis* or *trans* stereochemistry, are considered.

Heating *trans*-amine **3** with iodomethane or benzyl chloride in ethanol in the presence of K_2CO_3 gave the *N*,*N*-dimethyl salt **7** (75%) and the *N*-benzyl derivative **8** (71%), respectively. Treatment of compound **3** with an etheral solution of HCl yielded hydrochloride **3** · HCl (90%). The reaction with ethylene oxide (100 °C, 2 h, in a sealed tube) yielded *N*-(2-hydroxyethyl)-*trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine **9** (87%).

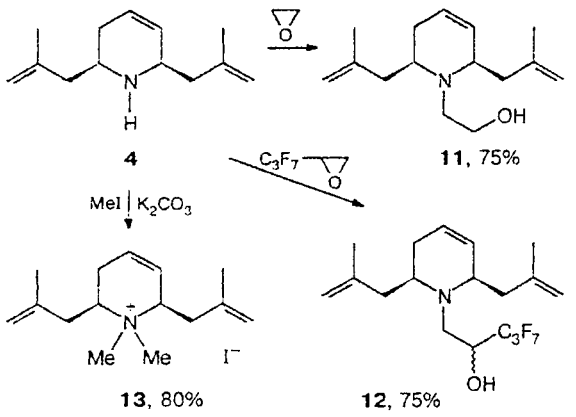


Opening of the epoxide ring in perfluoropropyloxirane under the action of **3**, as in the case of other secondary amines,[10] proceeded according to Krasusky's[10,11] rule to form aminoalcohol **10** (86%).



We succeeded in isolating two individual diastereoisomers of aminoalcohol (**10a** and **10b**) by column chromatography on neutral Al_2O_3 (L 40/250, a 10 : 1 hexane—ether mixture as the eluent). These diastereoisomers have different spectral characteristics (see Experimental). However, the stereochemistry of these diastereoisomers remains an open question.

Like **3**, *cis*-2,6-dimethallyl compound **4** readily forms the hydrochloride **4** · HCl. The reactions of **4** with ethylene oxide and perfluoropropyloxirane also proceed in the usual fashion to form the corresponding aminoalcohols **11** (78%) and **12** (75%, a ~1 : 1 mixture of two diastereoisomers, ^{19}F NMR).

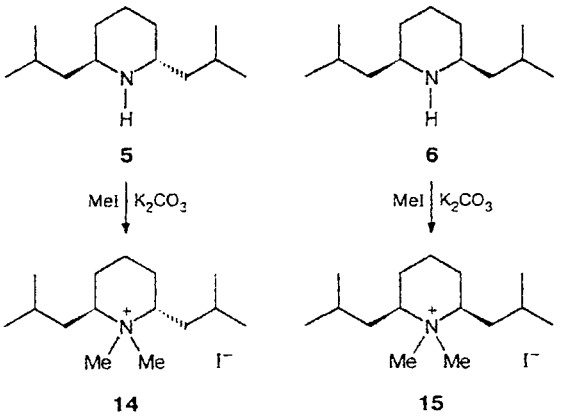


Heating amine **4** with MeI in the presence of K_2CO_3 in ethanol gave *N,N*-dimethyl salt **13** (80%). We failed to obtain the corresponding *N*-benzyl derivative of amine **4** using the standard procedure.

Stereochemistry of the products

In 1967, Kawazoe and coworkers[12] suggested a convenient method for determining the stereochemistry of *cis*- and *trans*-2,6-dimethylpiperidines and 2,5-dimethylpyrrolidines based on analysis of the ^1H NMR spectra of their *N,N*-dimethyl salts. In the corresponding salts of the *trans*-isomers, the methyl groups bonded to the nitrogen atom are equivalent and give a singlet in the ^1H NMR spectrum, whereas in the salts of the *cis*-isomers, the CH_3 groups are nonequivalent, and two singlets are observed in the spectrum. However, other researchers have not used this method much for many years. We confirmed the efficacy of this method when the demand arose for a determination of the stereochemistry of the products of the reductive diallylation of pyridines[5,7,8] and pyrrole[7,8] by triallylborane. We found that this problem can be solved using not only ^1H NMR spectroscopy but ^{13}C NMR spectroscopy as well.

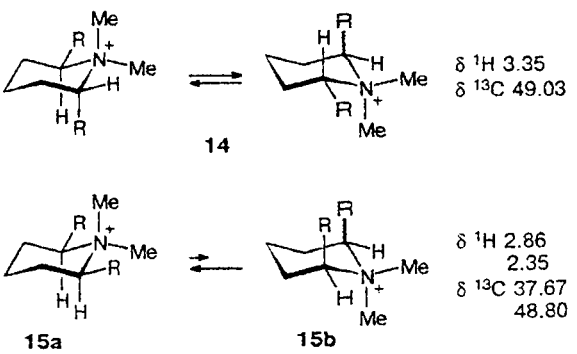
As mentioned above, hydrogenation of *trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (**3**) and *cis*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (**4**) over nickel in CH_3COOH gave *trans*-2,6-diisobutylpiperidine (**5**) and *cis*-2,6-diisobutylpiperidine (**6**), respectively. Heating hydrogenated amines with iodomethane in the presence of K_2CO_3 yielded *N,N*-dimethyl salts **14** and **15**. The reaction of compounds **5** and **6** with ethylene oxide (100 °C, 2 h, in a sealed tube) gave the corresponding aminoalcohols **16** and **17** (see below).



In *trans*-isomer **14**, both methyl groups bonded to the nitrogen atom are equivalent. The ^1H NMR spectrum has a singlet at δ 3.35 (6 H), while the ^{13}C NMR spectrum has one signal at δ 49.03. This unambiguously indicates that the isobutyl groups in amine **5** and, correspondingly, the methallyl substituents in compound **3** and in all its derivatives (**7**, **8**, **9**, and **10**) are in *trans* positions with respect to the ring.

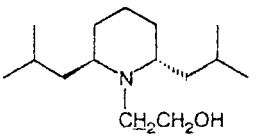
Two singlets of the CH_3 groups (at δ 2.86 and 3.35) and two signals (at δ 37.67 and 48.80) were observed in the ^1H and ^{13}C NMR spectra of *cis*-salt **15**, respectively, which indicates that these groups are nonequivalent (one group is in an axial position, and the second group is in an equatorial position).

In the case of *trans*-salt **14**, the two preferred chair-like conformations are identical: one isobutyl group is in an axial position, and the second group is in an equatorial position. Interconversion of these conformers (inversion of the ring) leads to a "one to itself" transformation. As a result of rapid inversion of the ring (at room temperature), the signals of the *N*-methyl groups are averaged. Apparently, in the case of salt **15**, conformation **15a** with an equatorial arrangement of the isobutyl

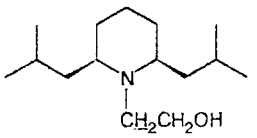


groups is preferred, whereas conformation **15b** is thermodynamically unfavorable for steric reasons (1,3-repulsion, *etc.*). In this salt (conformation **15a**), one *N*-methyl group is in an equatorial orientation, and the second group is in an axial orientation, *i.e.*, these groups are nonequivalent.

In the ^{1}H NMR spectrum of aminoalcohol **17**, the methylene protons (N—CH_2) appear as a pronounced triplet (δ 2.60, J = 6.1 Hz), which indicates that they are enantiotopic. This is additional supporting evidence for a *cis* arrangement of the 2,6-substituents with respect to the ring.



16



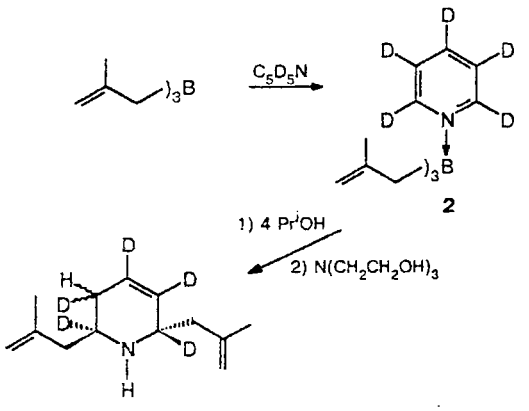
17

16: δ ^{1}H 2.5—2.95 (multiplet)
17: δ ^{1}H 2.6 (t, J = 6.1 Hz)

In the spectrum of aminoalcohol **16**, the signal of the N—CH_2 group is a multiplet (apparently, a triplet of quartets), which is indicative of their diastereotopism. In the case of aminoalcohols **16** and **17**, the multiplicity of the proton signals of the N—CH_2 group is more complex than in the case of the analogous *N*-benzyl derivatives due to the presence of adjacent protons (CH_2OH). However, the above-mentioned data indicate that products of the reaction with ethylene oxide (**16** and **17**) can also be used for determining the stereochemistry of *cis*- and *trans*-2,6-disubstituted piperidines. The structure of *N,N*-dimethyl salt **7** was established by X-ray structural analysis.[13]

Synthesis of pentadeuterated compounds

Treatment of the trimethallylborane complex of deuteropyridine **2** with 2-propanol (4 equiv., 20 °C, 2 h) and then with triethanolamine gave *trans*-2,6-di-(2-methylallyl)-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridine **18** in a yield of 82%.

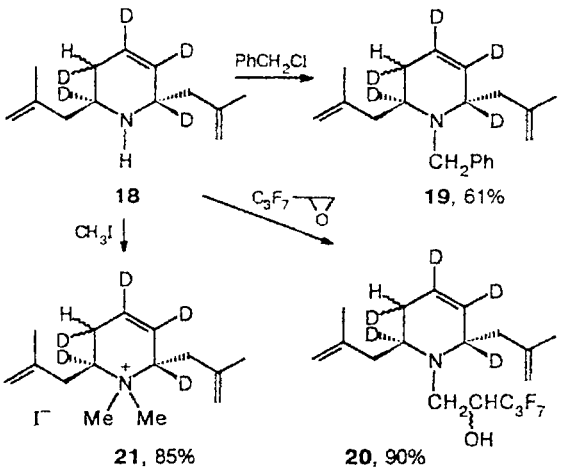


18, 82%

There is also no need to isolate adduct **2** in the pure form for preparing amine **18**. It is more convenient to prepare amine **18** *in situ* by mixing trimethallylborane and C_5D_5N in the ratio of 1 : 1 (without distillation) followed by treatment with 2-propanol.

The formation of amine **18** containing a hydrogen atom at position 3 of the heterocycle unambiguously indicates that alcohol (Pr^iOH) is involved in the **2**→**18** transformation. Analogous insertion of a proton or deuterium into the ring was observed previously when the complex of C_5D_5N with triallylborane was treated with methanol or deuteromethanol (CD_3OD), respectively.[5,7] These results are of considerable importance in understanding the mechanism of reductive *trans*-2,6-diallylation of pyridines with allylboranes.

N-benzyl derivative **19**, fluorinated aminoalcohol **20**, *N,N*-dimethyl salt **21**, and hydrochloride **18** · HCl were synthesized by the standard reactions using deuterated amine **18**. Compound **20** was obtained as a mixture of diastereoisomers, which were not separated.



Mechanism of reductive *trans*-diallylation of pyridines

The available data provide evidence that reductive *trans*-2,6-diallylation of pyridines with allylboranes is a general reaction that proceeds under mild conditions and is not complicated by side processes. The reaction is very convenient for experiments: all operations are carried out in a single flask (one-pot procedure), and the reagents (the corresponding pyridine, allylborane, alcohol, and alkali) are readily available.

However, from the chemical standpoint, it is a complex multistage process, and an understanding of its mechanism as a whole and of the individual stages is of great importance in revealing the optimum conditions of the synthesis of 2,6-diallylated products and in controlling their stereochemistry.

It is known[1—3] that pyridinium salts readily add nucleophilic reagents (OH^-, RO^-, RS^-, CN^-, NH_2^-,

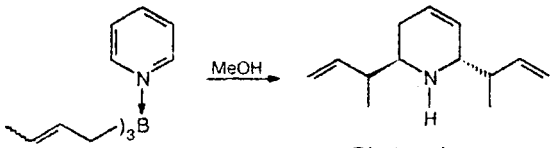
etc.) at position 2 or 4 of the ring. Considering that in the initially formed complexes $C_5H_5N \rightarrow BAll_3$, the nitrogen atom carries a positive charge (whereas the boron atom is negatively charged), we suggested a mechanism of reductive *trans*-diallylation that involves nucleophilic addition of the OR group at the α position of the pyridine ring.[4,7,8] However, later on (in particular, in the course of our studies), important data were obtained that allowed one to gain a more penetrating insight into the mechanism of the process.

The following facts are of prime importance:

1. The majority of the complexes of allylboranes with pyridine and its derivatives are thermally stable and remain unchanged with prolonged heating (160 °C under normal pressure[4] and under high pressure[8]).

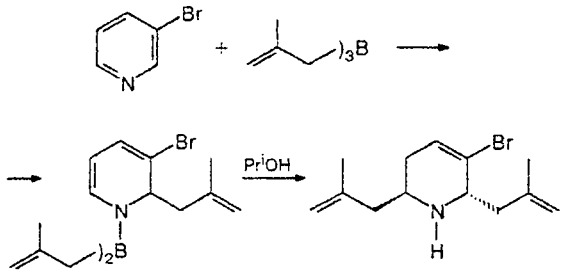
2. Alcohol (or H_2O or R_2NH) is involved in the process as a reagent (rather than as a solvent). The proton of ROH is localized at position 3 of the *trans*-2,6-diallylated product. This is confirmed by the reaction with deuterated compounds (C_5D_5N and CH_3OD).[5,8,14]

3. Addition of the first and second allyl groups to the heterocycle is accompanied by allylic rearrangement, as evidenced by the fact that amine with terminal double bonds is formed from tricrotylborane.[8,14]



Diastereoisomers
(20 : 19 : 1)

4. Trimethallylborane reacts with 3-bromopyridine to form a 1,2-addition product (b.p. 92—94 °C (1 Torr), δ ^{11}B 50.4). Treatment of the latter with 2-propanol yields the *trans*-2,6-dimethallyl derivative.[15]

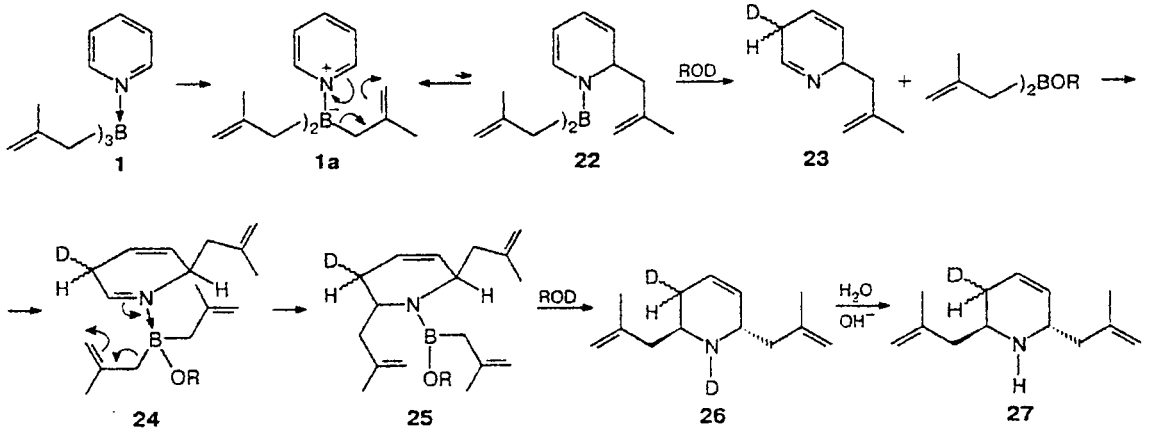


We failed to detect (NMR) the analogous product of 1,2-addition of triallylborane to 3-BrC_5H_4N. The reaction of triallylborane with 3-BrC_5H_4N yielded the 1 : 1 adduct, which was distilled *in vacuo* (b.p. 106 °C (1 Torr), δ ^{11}B −0.3).[8,14]

5. Trialkylboranes and tribenzylborane readily react with pyridine to form the corresponding 1 : 1 adducts $R_3B \cdot Py$. However, these compounds remain unchanged when treated with alcohols. Consequently, transformations of the pyridine complexes occur only in the case of boron-allyl compounds that can participate in reactions involving allylic rearrangements. These facts make it possible to propose a reasonable mechanism for the reductive *trans*-2,6-diallylation of pyridines (Scheme 1).

It is believed that reversible intramolecular allylboration of the double C=N bond occurs in complex **1** to form aminoborane **22**. Generally, the **1a** ⇌ **22** equilibrium is substantially shifted to the left, and at each instant of time only a very small amount of 1,2-addition product **22** is present in the mixture. The crucial role of alcohol consists in the cleavage of the B—N bond in aminoborane **22**, which is accompanied by the transfer of the double bond (allylic rearrangement) to form azomethine **23** and dimethallylboronic ester, which immediately react to form the corresponding (B←N) adduct. Stereospecific allylboration of the C=N bond of this adduct occurs through six-membered transition state **24**. The second allyl group is attached to the ring in a

Scheme 1



1 **1a** **22** **23** **24** **25** **26** **27**

trans position with respect to the first group. The new aminoborane **25** formed is deborated with alcohol to give amine **26** and methallylboronic ester. The latter is separated from amine **26** by treating the mixture with an alkaline solution because it forms the borate complex $[RB(OH)_3]Na$ (or the product of its hydrolysis, boric acid), which is transferred to the aqueous layer. In the course of this treatment, the deuterium at the nitrogen atom is replaced by hydrogen to form the final product (compound **27** in Scheme 1).

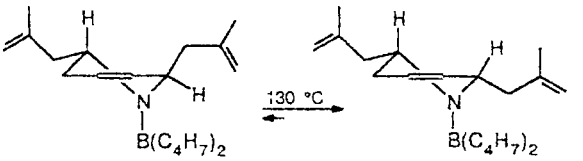
An understanding of the mechanism of reductive *trans*-2,6-diallylation of pyridines made it possible to develop a convenient method for the synthesis of *trans*-2,6-unsymmetrically substituted Δ^3-piperideines and piperidines that involves 1,2-addition of RLi to pyridine followed by *trans*-allylation with triallylborane.[16]

Mechanism of *trans*→*cis* isomerization

As mentioned above, when heated with trimethallylborane (130—135 °C, 2 h), *trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine **3** is almost quantitatively transformed into *cis*-isomer **4**. The possible mechanism of isomerization is shown in Scheme 2.

The reaction of secondary amine **3** with trimethallylborane yields the (B←N) complex, which is formed *via* the electron pair of the nitrogen atom and the unoccupied p-orbital of the boron atom. Then, when the adduct is slightly heated, one B—C bond is cleaved, isobutylene is eliminated, and aminoborane **28** with a *trans* arrangement of the methyl groups forms. The latter is transformed into *cis*-aminoborane **31** at 130 °C. Transformation **28**→**31** occurred, apparently, through reversible deallylboration—allylboration (elimination—addition of the B—methallyl fragment) *via* six-membered transition states with cyclic electron transfer (**28** and **30**). Most likely, the 6-methallyl group (rather than 2-C_4H_7) is involved in the elimination—addition process because a system of conjugated bonds is formed (**29**) due to migration of this group to the boron atom of the ring. Subsequent allylboration of the C=N bond in compound **29** yields *cis*-aminoborane **31**.

Isomer **31** with two pseudoequatorial methallyl groups exhibits higher thermodynamic stability than *trans*-isomer **28** in which one methallyl group occupies an equatorial position and the second group is in a pseudoaxial position. This high stability is a driving force of **28**→**31** isomerization



28 **31**

Treatment of aminoborane **31** with methanol and alkali (deboronation) gave free amine **4** in almost quantitative yield.

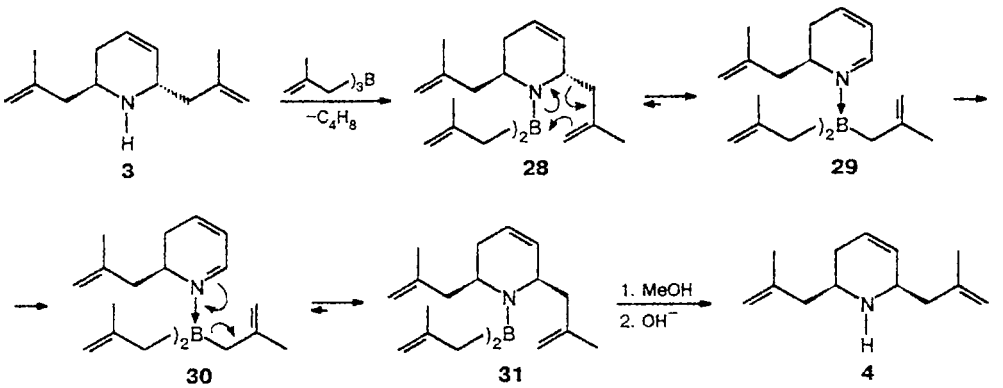
Therefore, we have demonstrated that reductive *trans*-diallylation of pyridine and its derivatives with trimethallylborane proceeds under milder conditions (20 °C) than the analogous reactions with the participation of triallylborane. Using this available boron reagent, *trans*- and *cis*-2,6-dimethallyl-Δ^3-piperideines, *cis*- and *trans*-2,6-diisobutylpiperidines, and many their derivatives can be readily prepared. A research program along this line is in progress, and we shall concentrate our attention on extension of the field of application of this reaction in organic synthesis and the use of this reaction as the key stage in the synthesis of a number of alkaloids.

Experimental

All operations with organoboron compounds were carried out under an atmosphere of dry argon. The ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded on a Bruker AC-200P spectrometer. The chemical shifts (the δ scale) are given relative to Me_4Si, $CFCl_3$, and $BF_3 \cdot OEt_2$. The IR spectra were obtained on an UR-20 spectrometer. Absolute solvents were used. Trimethallylborane was synthesized according to the procedure reported previously.[17]

The complex of trimethallylborane with pyridine (1) was prepared by adding pyridine to trimethallylborane taken in the

Scheme 2



ratio of 1 : 1, b.p. 75—77 °C (1 Torr), n_D^{19} = 1.5370. Found (%): C, 80.08; H, 10.37; B, 4.23. $C_{17}H_{26}BN$. Calculated (%): C, 80.01; H, 10.27; B, 4.24. ^{1}H NMR ($CDCl_3$), δ: 1.60 (s, 15 H, CH_3 and CH_2); 4.1—4.55 (6 H, 3 CH_2=C); 7.47 (2 H, 3- and 5-H of pyridine); 7.86 (1 H, 4-H of pyridine); 8.55 (2 H, 2- and 6-H of pyridine). ^{13}C NMR ($CDCl_3$), δ: 26.16 (CH_3); 35.62 (CH_2); 107.49 (=CH_2); 124.21 (C(3) and C(5) of pyridine); 138.80 (C(4) of pyridine); 145.33 (C(2) and C(6) of pyridine); 149.69 (=C—). ^{11}B NMR ($CDCl_3$), $\delta_{BF_3\cdot OEt_2}$: −0.5.

The complex of trimethallylborane with deuteropyridine (2) was prepared analogously to complex **1**, b.p. 81—82 °C (1.5 Torr), $n_D^{20.5}$ = 1.5345. Found (%): C, 78.73; H, 8.36; D, 3.98; B, 4.38. $C_{17}H_{21}D_5BN$. Calculated (%): C, 78.48; H, 8.14; D, 3.84; B, 4.15. ^{1}H NMR ($CDCl_3$), δ: 1.60 (s, 15 H, CH_3 and CH_2); 4.1—4.5 (6 H, 3 CH_2=C). ^{2}H NMR ($CDCl_3$), δ: 7.57 (2 H, 3- and 5-H of pyridine); 7.96 (1 H, 4-H of pyridine); 8.64 (2 H, 2- and 6-H of pyridine). ^{13}C NMR ($CDCl_3$), δ: 26.18 (CH_3); 35.65 (CH_2); 107.46 (=CH_2); 123.71 (t, C(3) and C(5), $^1J_{^{13}C-^2H}$ = 26.2 Hz); 138.35 (t, C(4), $^1J_{^{13}C-^2H}$ = 24.7 Hz); 144.98 (t, C(2) and C(6), $^1J_{^{13}C-^2H}$ = 27.6 Hz); 149.82 (=C—). ^{11}B NMR ($CDCl_3$), $\delta_{BF_3\cdot OEt_2}$: −0.7.

***trans*-2,6-Dimethallyl-1,2,3,6-tetrahydropyridine (3).** Trimethallylborane (7.17 g, 40.7 mmol) was placed in a three-neck flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an inlet for argon. Pyridine (6.6 mL, 81.5 mmol) was added. The temperature was kept not higher than 25 °C. Then 2-propanol (12.4 mL, 161.9 mmol) was added at 20 °C. The mixture was stirred at room temperature for 2 h. Then the mixture was treated with a 10% NaOH solution (21.8 mL), intensely stirred for 30 min, extracted with ether, and dried with K_2CO_3. Distillation gave compound **3** (6.74 g, 87%), b.p. 62—63 °C (1 Torr), n_D^{22} = 1.4880. Found (%): C, 81.09; H, 10.90; N, 7.51. $C_{13}H_{21}N$. Calculated (%): C, 81.61; H, 11.06; N, 7.32. IR (thin layer, ν/cm^{-1}): 893, 1646, 3025, 3075 (CH_2=C and R^1CH=CHR^2); 1120, 3320 (C—NH). ^{1}H NMR ($CDCl_3$), δ: 1.74 (6 H, 2 CH_3); 1.80—2.32 (m, 1 H, N—H and 6 H, CH_2—C=); 3.0 (m, 1 H, C(2)—H); 3.54 (m, 1 H, C(6)—H); 4.64—4.92 (4 H, CH_2=C); 5.56—5.84 (2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 21.47, 21.66 (CH_3); 31.84 (C-3); 42.65, 44.28 (CH_2); 43.39, 49.37 (C-2,6); 112.58 (=CH_2); 124.42, 129.18 (C-4,5); 141.60, 142.04 (=C—).

Hydrochloride 3·HCl was prepared from compound **3** (1.32 g) and an ethereal solution of HCl in a yield of 1.41 g (90%), m.p. 194—195.5 °C (from an ether—methanol mixture). Found (%): C, 68.05; H, 9.65; N, 5.99; Cl, 15.40. $C_{13}H_{22}NCl$. Calculated (%): C, 68.55; H, 9.74; N, 6.15; Cl, 15.56. IR (KBr pellets, ν/cm^{-1}): 901, 1647, 3075 (CH_2=C and R^1CH=CHR^2); 1585, 2720 (NH_2^+). ^{1}H NMR ($CDCl_3$), δ: 1.76, 1.80 (s, 6 H, 2 CH_3); 2.18—2.64 (4 H, CH_2—C=); 2.78—3.08 (2 H, CH_2—C=); 3.6 (m, 1 H, C(2)—H); 3.98 (br.s, 1 H, C(6)—H); 4.72—5.04 (4 H, CH_2=C); 5.62—5.98 (2 H, CH=CH); 9.6 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 21.99, 22.21 (CH_3); 26.04 (C-3); 39.15, 40.79 (CH_2); 47.70, 48.85 (C-2,6); 114.72, 115.05 (=CH_2); 123.38, 124.61 (C-4,5); 139.07, 139.37 (=C—).

***cis*-2,6-Dimethallyl-1,2,3,6-tetrahydropyridine (4).** Trimethallylborane (6.08 g, 34.5 mmol) was placed in a three-neck flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an inlet for argon. *trans*-2,6-Dimethallyl-1,2,3,6-tetrahydropyridine **3** (6.74 g, 35.2 mmol) was added. The reaction mixture was heated at 130—135 °C for 2.5 h. Then methanol (1.43 mL) and a 10% NaOH solution (18.5 mL) were added successively to the reaction mixture with cooling. The mixture was refluxed for 1 h, extracted with ether, and dried with potassium carbonate. Distillation gave compound **4** (6.27 g, 93%), b.p. 60—63 °C (2 Torr). An admixture of the *trans*-isomer (5—6%) was separated on a column with Al_2O_3 (neutral L 40/250); a 30 : 1 hexane—ether mixture was used as the eluent. Pure compound **4** was obtained, b.p. 43—44 °C (0.5 Torr), n_D^{20} = 1.4849. Found (%): C, 81.57; H, 11.06. $C_{13}H_{21}N$. Calculated (%): C, 81.61; H, 11.06; N, 7.32. IR (thin layer, ν/cm^{-1}): 896, 1650, 3030, 3080 (CH_2=C and R^1CH=CHR^2); 1121, 3330 (C—NH). ^{1}H NMR ($CDCl_3$), δ: 1.5—2.2 (13 H, 2 CH_3, NH and 3 CH_2—C=); 2.89, 3.47 (m, 2 H, C(2)—H and C(6)—H); 4.6—4.9 (m, 4 H, CH_2=C); 5.5—5.9 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 21.27, 21.44 (CH_3); 32.03 (C-3); 43.67, 43.97 (CH_2); 49.42, 51.62 (C-2,6); 111.66, 112.11 (=CH_2); 124.48, 129.52 (C-4,5); 141.06 (=C—).

Hydrochloride 4·HCl was prepared from compound **4** (1.13 g, 5.9 mmol) and a solution of HCl in diethyl ether in a yield of 1.28 g (95%), m.p. 228.5—230 °C (from an ether—methanol mixture). Found (%): C, 68.97; H, 9.91; N, 6.19; Cl, 15.57. $C_{13}H_{22}NCl$. Calculated (%): C, 68.55; H, 9.74; N, 6.15; Cl, 15.56. ^{1}H NMR ($CDCl_3$), δ: 1.73 (s, 3 H, CH_3); 1.76 (s, 3 H, CH_3); 2.20—2.70 (m, 4 H, CH_2—C=); 3.05 (m, 2 H, CH_2—C=); 3.39, 3.99 (m, 2 H, C(2)—H and C(6)—H); 4.85 (m, 4 H, CH_2=C); 5.6—6.0 (m, 2 H, CH=CH); 9.8 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 22.16, 22.37 (CH_3); 28.02 (C-3); 40.24, 41.08 (CH_2); 53.09, 53.31 (C-2,6); 114.48 (=CH_2); 123.47, 125.76 (C-4,5); 139.15, 139.29 (=C—).

***trans*-2,6-Diisobutylpiperidine (5).** Compound **3** (4.11 g, 21.5 mmol), acetic acid (16.3 mL), and Raney nickel (0.1 g) were placed in a 0.5-L autoclave. Then H_2 (100 atm.) was introduced. The reaction mixture was heated at 95—100 °C for 13 h. The nickel was separated, and a 20% NaOH solution was added until the acetic acid was completely neutralized. The mixture was extracted with ether and dried with K_2CO_3. Distillation gave compound **5** (3.60 g, 85%), b.p. 65—66 °C (1 Torr), n_D^{20} = 1.4540. Found (%): C, 78.82; H, 13.53. $C_{13}H_{27}N$. Calculated (%): C, 79.11; H, 13.79; N, 7.10. IR (thin layer, ν/cm^{-1}): 717, 1366, 1382, 1465, 2870, 2925, 2952. ^{1}H NMR ($CDCl_3$), δ: 0.8—1.02 (12 H, CH_3); 1.05—1.8 (w.m, ^{13}H, CH in Bu^i, NH, CH_2); 2.93 (m, 2 H, C(2)—H and C(6)—H). ^{13}C NMR ($CDCl_3$), δ: 19.72 (C-4); 22.23, 23.18, 24.51 (CH_3 and CH in Bu^i); 31.56 and 43.50 (C-3,5 and CH_2 in Bu^i); 47.92 (C-2,6).

Hydrochloride 5·HCl was prepared from compound **5** (0.2 g, 1.01 mmol) and an ethereal solution of HCl in a yield of 0.22 g (93%), m.p. 228—229.5 °C (from an ether—methanol mixture). Found (%): C, 66.92; H, 12.21; Cl, 15.34. $C_{13}H_{28}NCl$. Calculated (%): C, 66.78; H, 12.07; N, 5.99; Cl, 15.16. ^{1}H NMR ($CDCl_3$), δ: 0.85—1.1 (12 H, CH_3); 1.5—2.2 (w.m, 12 H, CH in Bu^i, CH_2); 3.36 (m, 2 H, C(2)—H and C(6)—H); 9.31 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 17.33 (C-4); 21.18, 23.33, 24.44 (CH_3 and CH in Bu^i); 26.11 and 38.87 (C-3,5 and CH_2 in Bu^i); 50.25 (C-2,6).

***cis*-2,6-Diisobutylpiperidine (6).** Compound **4** (3.03 g, 15.8 mmol), acetic acid (12 mL), and Raney nickel (0.05 g) were placed in a 0.5 L autoclave. Then H_2 (95 atm) was introduced. The reaction mixture was heated at 95—100 °C for 10 h. The nickel was separated, and a 20% NaOH solution was added until the acetic acid was completely neutralized. The organic layer was separated, and the water layer was extracted with ether. The ethereal extracts were combined and dried with K_2CO_3. Distillation gave compound **6** (2.49 g, 80%), b.p. 65—67 °C (2 Torr), n_D^{15} = 1.4520. Found (%):

C, 79.13; H, 13.74. $C_{13}H_{27}N$. Calculated (%): C, 79.11; H, 13.79; N, 7.10. IR (thin layer, ν/cm^{-1}): 732, 1312, 1333, 1369, 1385, 1453, 1467, 2870, 2929, 2955. ^1H NMR ($CDCl_3$), δ: 0.88 (d, 6 H, 2 CH_3); 0.91 (d, 6 H, 2 CH_3); 0.94—1.85 (w.m, 13 H, CH in Bu^i, NH, CH_2); 2.45—2.65 (m, 2 H, C(2)—H and C(6)—H). ^{13}C NMR ($CDCl_3$), δ: 22.28, 23.02, 24.11 (CH_3 and CH in Bu^i); 24.82, 32.97 and 46.39 (C-3,4,5 and CH_2 in Bu^i); 54.45 (C-2,6).

Hydrochloride 6 · HCl, m.p. 245.5—246.5 °C (from an ether—methanol mixture). Found (%): C, 66.94; H, 12.15; Cl, 15.00. $C_{13}H_{28}NCl$. Calculated (%): C, 66.78; H, 12.07; N, 5.99; Cl, 15.16. ^1H NMR ($CDCl_3$), δ: 0.90 (d, 6 H, 2 CH_3); 0.97 (d, 6 H, 2 CH_3); 1.35—2.2 (w.m, 12 H, CH and CH_2); 2.85—3.15 (m, 2 H, C(2)—H and C(6)—H); 8.90—9.35 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 20.95, 24.09, 24.63 (CH_3 and CH in Bu^i); 23.08, 27.88, 40.95 (C-3,4,5 and CH_2 in Bu^i); 57.95 (C-2,6).

***trans*-2,6-Dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide (7).** A mixture of compound **3** (0.94 g, 4.9 mmol), MeI (1.24 mL, 19.6 mmol), K_2CO_3 (1.38 g, 9.8 mmol), and ethanol (10 mL) was refluxed for 5 h. The solution was filtered and evaporated to dryness *in vacuo*. The residue was extracted with chloroform, filtered, and evaporated *in vacuo*. Crystallization of the residue from an ethyl acetate—EtOH mixture gave salt **7** (1.28 g, 75%), m.p. 164—165 °C. Found (%): C, 51.60; H, 7.68; N, 4.01; I, 36.75. $C_{15}H_{26}NI$. Calculated (%): C, 51.88; H, 7.55; N, 4.03; I, 36.54. IR (KBr pellets, ν/cm^{-1}): 895, 916, 1647, 3005, 3075 (C=CH_2 and R^1CH=CHR^2). ^1H NMR ($CDCl_3$), δ: 1.9 (s, 6 H, 2 CH_3); 2.2—3.06 (m, 6 H, CH_2); 3.4 (s, 3 H, N^+—CH_3); 3.58 (s, 3 H, N^+—CH_3); 4.08—4.34 (m, 2 H, C(2)—H and C(6)—H); 4.82—5.06 (4 H, CH_2=); 5.62—6.04 (2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 22.48, 22.53 (CH_3); 25.28 (C-3); 35.70, 36.43 (CH_2); 47.43, 49.49 (N^+—CH_3); 64.75, 66.04 (C-2,6); 115.65, 116.02 (=CH_2); 122.29, 123.55 (C-4,5); 137.95, 138.71 (=C—).

1-Benzyl-*trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (8). A mixture of compound **3** (3.68 g, 19.3 mmol), benzyl chloride (2.22 mL, 19.3 mmol), K_2CO_3 (5.34 g, 38.6 mmol), and ethanol (10 mL) was refluxed for 5 h. EtOH was distilled off *in vacuo*. Then water was added to the reaction mixture until the K_2CO_3 was completely dissolved. The mixture was extracted with ether and dried with K_2CO_3. Distillation gave compound **8** (3.84 g, 71%), b.p. 129—129.5 °C (1.5 Torr), $n_D^{22.5}$ = 1.5290. Found (%): C, 85.01; H, 9.57; N, 4.68. $C_{20}H_{27}N$. Calculated (%): C, 85.35; H, 9.67; N, 4.98. IR (thin layer, ν/cm^{-1}): 890, 1645, 3022, 3072 (CH_2=C and R_1CH=CHR_2); 704, 738, 1495, 1600, 1775, 1865, 1940 (Ph—); 1117 (C—N). ^1H NMR ($CDCl_3$), δ: 1.44, 1.74 (s, 6 H, 2 CH_3); 1.9 (m, 2 H, C(3)—H); 2.0—2.4 (4 H, CH_2—C=); 3.0—3.3 (m, 2 H, C(2)—H and C(6)—H); 3.59 (AB-spectrum, δ_A = 3.42; δ_B = 3.76; J_{AB} = 13.43 Hz; 2 H, CH_2Ph); 4.5—4.85 (m, 4 H, CH_2=C); 5.5—5.86 (2 H, CH=CH); 7.05—7.4 (5 H, Ph). ^{13}C NMR ($CDCl_3$) δ: 22.18 (CH_3); 26.43 (C-3); 40.32, 43.19 (CH_2); 49.51, 55.23 (C-2,6); 50.26 (N—C—Ph); 111.97, 112.08 (CH_2=); 124.90, 129.00 (C-4,5); 126.40, 127.81, 128.76, 140.66 (Ph); 143.16, 143.57 (=C—).

***N*-(2′-Hydroxyethyl)-*trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (9).** Compound **3** (3.14 g, 16.6 mmol), MeOH (9 mL), a 15% excess of ethylene oxide, and concentrated HCl (0.04 mL) were placed in a tube. The reaction mixture was heated at 100 °C for 2 h. After cooling, the low-boiling compounds were distilled off, and an excess of a 20% NaOH solution and ether were added. The mixture was intensely shaken, and the ethereal layer was separated. The aqueous layer was extracted three times with ether. The ethereal extracts were dried with K_2CO_3. Distillation gave compound **9** (3.39 g, 87%), b.p. 106—107 °C (1 Torr), n_D^{20} = 1.5000. Found (%): C, 76.35; H, 10.58. $C_{15}H_{25}NO$. Calculated (%): C, 76.54; H, 10.71; N, 5.95. IR (thin layer, ν/cm^{-1}): 890, 1642, 3020, 3070 (CH_2=C and R^1CH=CHR^2); 1118 (C—N); 1060, 3440 (br.) (C—OH). ^1H NMR ($CDCl_3$), δ: 1.69 (s, 3 H, CH_3); 1.72 (s, 3 H, CH_3); 1.75—1.9 (2 H, C(3)—H); 2.0—2.45 (4 H, CH_2—C= and 1 H N—CH_2); 2.63—2.8 (1 H, N—CH_2); 3.0—3.24 (3 H, C(2)—H, C(6)—H and OH); 3.32—3.60 (2 H, CH_2—O); 4.63—4.83 (4 H, CH_2=C); 5.52—5.86 (2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 21.86, 21.91 (CH_3); 25.89 (C-3); 40.95, 42.16, 46.76 (CH_2 in methallyl groups and N—CH_2); 48.51, 56.16 (C-2,6); 58.04 (CH_2—OH); 112.00, 112.20 (=CH_2); 125.51, 128.25 (C-4,5); 142.24, 142.66 (=C—).

***N*-(2′-Heptafluoropropyl-2′-hydroxyethyl)-*trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (10).** A mixture of compounds **3** (2.67 g, 14.0 mmol) and heptafluoropropylethylene oxide (2.99 g, 14.1 mmol) was heated at 120—130 °C for 2 h. Distillation gave a mixture of diastereoisomers **10a,b** (4.83 g, 86%), b.p. 103—104 °C (1 Torr). Both diastereoisomers were isolated in the pure form by column chromatography on Al_2O_3 (neutral L 40/250); a 10 : 1 hexane—ether mixture was used as the eluent.

Compound 10a: ^1H NMR ($CDCl_3$), δ: 1.77 (s, 6 H, 2 CH_3); 1.85—2.45 (m, 6 H, CH_2—C=); 2.5—3.2 (m, 2 H, N—CH_2); 3.13, 3.28 (both m, 2 H, C(2)—H and C(6)—H); 4.08 (w.m, 1 H, CH—CF_2); 4.40 (br.s, 1 H, OH); 4.7—4.95 (m, 4 H, CH_2=C—); 5.55—6.0 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 22.11, 22.21 (CH_3); 26.70 (C-3); 41.52, 42.62, 43.50 (CH_2 in methallyl groups and N—CH_2); 48.88, 57.03 (C-2,6); 64.59 (d.d, (CH—OH), $^2J_{^{13}C-^{19}F_A}$ = 28.3 Hz and $^2J_{^{13}C-^{19}F_B}$ = 22.1 Hz); 113.28, 113.41 (=CH_2); 126.46, 127.80 (C-4,5); 141.79, 142.41 (=C—). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.76 (m, 3 F, CF_3); −126.38 (m, 2 F, CF_2—CF_3); the AB-spectrum: δ_A = −124.5, δ_B = −128.5, J_{AB} = 282.4 Hz (CF_2—CH(OH)).

Picrate of 10a. The reaction of compound **10a** (0.35 g, 0.9 mmol) and picric acid (0.2 g, 0.9 mmol) in ethanol gave the picrate (0.5 g, 91%), m.p. 129—130 °C (from an ether—methanol mixture). ^1H NMR ($CDCl_3$), δ: 1.70 (s, 3 H, CH_3); 1.85 (s, 3 H, CH_3); 2.0—2.9 (m, 6 H, 3CH_2—C=); 3.4 (m, 2 H, N—CH_2); 4.15 (m, 2 H, C(2)—H and CH—CF_2); 4.90 (m, 5 H, 2 CH_2=C— and C(6)—H); 5.90 (m, 2 H, CH=CH); 8.85 (s, 2 H, Ar—). ^{13}C NMR ($CDCl_3$), δ: 22.2, 22.28 (CH_3); 24.96 (C-3); 39.00, 40.93, 49.14 (CH_2 in methallyl groups and N—CH_2); 54.92, 61.12 (C-2,6); 64.66 (d.d, (CH—OH), $^2J_{^{13}C-^{19}F_A}$ = 29.0 Hz and $^2J_{^{13}C-^{19}F_B}$ = 22.0 Hz); 116.04 (=CH_2); 122.24, 125.49 (C-4,5); 137.98, 138.13 (=C—); 126.67, 129.55, 141.59, 161.37 (Ar—). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.32 (m, 3 F, CF_3); AB-spectrum: δ_A = −124.6, δ_B = −126.3, J_{AB} = 295.2 Hz (2 F, CF_2—CF_3); the AB-spectrum: δ_A = −118.3, δ_B = −126.9, J_{AB} = 285.0 Hz (CF_2—CH(OH)).

Compound 10b: ^1H NMR ($CDCl_3$), δ: 1.65 (s, 3 H, CH_3); 1.70 (s, 3 H, CH_3); 1.80—2.4 (m, 6 H, CH_2—C=); 2.55, 2.97 (both m, 2 H, N—CH_2); 3.13 (w.m, 2 H, C(2)—H and C(6)—H); 3.94 (w.m, 1 H, CH—CF_2); 4.5—4.93 (m, 5 H, 2 CH_2=C— and —OH); 5.5—5.85 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 22.14, 22.19 (CH_3); 26.00 (C-3); 40.67, 42.76, 46.24 (CH_2 in methallyl groups and N—CH_2); 49.53, 60.18 (C-2,6); 65.85 (d.d, (CH—OH), $^2J_{^{13}C-^{19}F_A}$ = 28.8 Hz and $^2J_{^{13}C-^{19}F_B}$ = 21.4 Hz); 112.77, 113.56 (=CH_2); 125.43, 129.12 (C-4,5); 142.09, 142.78 (=C—). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.76 (m, 3 F, CF_3); −126.18 (m, 2 F,

CF_2—CF_3); the AB-spectrum: δ_A = −124.0, δ_B = −128.5, J_{AB} = 278.8 Hz (CF_2—CH(OH)).

Picrate of 10b. The reaction of compound **10b** (0.17 g, 0.4 mmol) with picric acid (0.1 g, 0.4 mmol) in ethanol gave the picrate (0.24 g, 90%), m.p. 133—134 °C (from an ether—methanol mixture). ^{1}H NMR ($CDCl_3$), δ: 1.75 (s, 3 H, CH_3); 1.85 (s, 3 H, CH_3); 2.1—3.0 (w.m, 6 H, 3 CH_2—C=); 3.4 (w.m, 2 H, N—CH_2); 4.1 (m, 1 H, CH—CF_2); 4.5, 5.18 (m, 2 H, C(2)—H and C(6)—H); 4.90 (m, 4 H, 2 CH_2=C—); 5.93 (m, 2 H, CH=CH); 9.0 (s, 2 H, Ar—). ^{13}C NMR ($CDCl_3$), δ: 22.07 (CH_3); 24.89 (C-3); 29.57, 38.92, 40.94 (CH_2 in methallyl groups and N—CH_2); 48.16, 55.2 (C-2,6); 66.27 (d.d, (CH—OH), $^2J_{^{13}C-^{19}F_A}$ = 28.4 Hz and $^2J_{^{13}C-^{19}F_B}$ = 21.3 Hz); 115.74, 116.04 (=CH_2); 122.36, 124.86 (C-4,5); 137.88, 138.05 (=C—); 126.83, 131.17, 140.29, 159.62 (Ar—). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.4 (m, 3 F, CF_3); AB-spectrum: δ_A = −124.6, δ_B = −126.0, J_{AB} = 294.7 Hz (2 F, CF_2—CF_3); the AB-spectrum: δ_A = −119.08, δ_B = −126.8, J_{AB} = 290.8 Hz (CF_2—CH(OH)).

***N*-(2′-Hydroxyethyl)-*cis*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (11)** was prepared analogously to **9** from compound **4** (1.10 g, 5.7 mmol), MeOH (3 mL), ethylene oxide (15% excess), and concentrated HCl (0.02 mL) with heating at 100 °C for 2 h. After cooling, the low-boiling compounds were distilled off, and an excess of a 20% NaOH solution and ether were added. The reaction mixture was thoroughly shaken, and the ethereal layer was separated. The aqueous layer was extracted three times with ether. The ethereal extracts were dried with K_2CO_3. The yield was 1.06 g (78%), b.p. 115—116 °C (1 Torr), n_D^{21} = 1.5062. Found (%): C, 76.66; H, 10.61. $C_{15}H_{25}NO$. Calculated (%): C, 76.54; H, 10.71. IR (thin layer, ν/cm^{-1}): 895, 1644, 1648, 3030, 3072 (CH_2=C and R^1CH=CHR^2); 1050, 3410 (br.) (C—OH). ^{1}H NMR ($CDCl_3$), δ: 1.70 (s, 3 H, CH_3); 1.74 (s, 3 H, CH_3); 1.8—2.65 (6 H, CH_2—C=); 2.7—3.0 (2 H, N—CH_2); 3.15—3.8 (5 H, C(2)—H, C(6)—H, OH, and CH_2—O); 4.6—5.0 (4 H, CH_2=C); 5.5—6.0 (2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 22.35 (CH_3); 24.66 (C-3); 42.70, 43.69, 54.02 (CH_2 in methallyl groups and N—CH_2); 54.32, 56.99 (C-2,6); 59.38 (CH_2—OH); 112.29, 112.88 (=CH_2); 123.74, 128.37 (C-4,5); 143.19, 143.49 (=C—).

***N*-(2′-Heptafluoropropyl-2′-hydroxyethyl)-*cis*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (12).** A mixture of compound **4** (1.64 g, 8.6 mmol) and heptafluoropropylethylene oxide (1.86 g, 8.8 mmol) was heated at 115—135 °C for 6 h; the temperature was gradually increased from 115 °C to 135 °C as oxide was consumed. Distillation gave a mixture of diastereoisomers **12** (58 : 42) in a yield of 2.59 g (75%), b.p. 112—113 °C (1 Torr). This mixture crystallized upon storage. We failed to isolate diastereoisomers in the individual form. The spectra of the mixture of two diastereoisomers are given below. ^{1}H NMR ($CDCl_3$), δ: 1.70 (s, 3 H, CH_3); 1.73 (s, 3 H, CH_3); 1.9—2.5 (w.m, 6 H, 3 CH_2—C=); 2.5—3.6 (w.m, 4 H, C(2)—H, C(6)—H and N—CH_2); 4.03 (m, 1 H, CH—CF_2); 4.60 (br.s, 1 H, OH); 5.2 (m, 4 H, CH_2=C—); 5.75 (m, 2 H, CH=CH). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.6 (m, 3 F, CF_3); −126.4 (m, 2 F, CF_2—CF_3); the AB-spectrum: δ_A = −124.6, δ_B = −128.9, J_{AB} = 279.1 Hz, and the AB-spectrum: δ_A = −125.1, δ_B = −129.2, J_{AB} = 284.1 Hz (2 F, CF_2—CH(OH)).

***cis*-2,6-Dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide (13).** A mixture of compound **4** (0.59 g, 3.1 mmol), MeI (0.77 mL, 12.3 mmol), K_2CO_3 (0.85 g, 6.2 mmol), and ethanol (10 mL) was refluxed for 5 h. The reaction mixture was filtered. The solution was evaporated to dryness *in vacuo*. The residue was extracted with chloroform, filtered, and evaporated *in vacuo*. The raw product was washed with hexane and ether. Salt **13** (0.86 g, 80%), m.p. 101—103 °C was obtained. Found (%): C, 51.76; H, 7.54; I, 36.20. $C_{15}H_{26}NI$. Calculated (%): C, 51.88; H, 7.55; N, 4.03; I, 36.54. ^{1}H NMR ($CDCl_3$), δ: 1.88 (s, 3 H, CH_3); 1.93 (s, 3 H, CH_3); 2.05—2.6 (4 H, CH_2); 2.88 (s, 3 H, N^+—CH_3); 2.85—3.02 (2 H, CH_2); 3.57 (s, 3 H, N^+—CH_3); 4.59 (m, 1 H, C(2)—H); 4.85—5.2 (5 H, 2CH_2= and C(6)—H); 5.62 (d, 1 H, CH=); 5.90—6.08 (m, 1 H, CH=). ^{13}C NMR ($CDCl_3$), δ: 22.51, 22.60 (CH_3); 26.79 (C-3); 36.50, 36.72 (CH_2); 38.82, 48.35 (N^+—CH_3); 67.91, 68.54 (C-2,6); 115.98 (=CH_2); 122.43, 124.86 (C-4,5); 138.46, 138.58 (=C—).

***trans*-2,6-Diisobutyl-1,1-dimethylpiperidinium iodide (14).** A mixture of compound **5** (0.46 g, 2.3 mmol), MeI (0.6 mL, 9.3 mmol), K_2CO_3 (0.64 g, 4.7 mmol), and ethanol (10 mL) was refluxed for 5 h. The reaction mixture was filtered. The solution was evaporated to dryness *in vacuo*. The residue was extracted with chloroform, filtered, and evaporated *in vacuo*. Crystallization from an ethyl acetate—EtOH mixture gave salt **14** (0.61 g, 74%), m.p. 196.5—197 °C. Found (%): C, 50.87; H, 9.10; N, 3.93; I, 36.05. $C_{15}H_{32}NI$. Calculated (%): C, 50.99; H, 9.13; N, 3.96; I, 35.92. ^{1}H NMR ($CDCl_3$), δ: 0.9—1.15 (12 H, CH_3); 1.55—2.3 (w.m, 12 H, CH in Bu^i, CH_2); 3.35 (s, 6 H, N^+—CH_3); 3.63 (m, 2 H, C(2)—H and C(6)—H). ^{13}C NMR ($CDCl_3$), δ: 16.42 (C-4); 21.38, 23.67, 25.63 (CH_3 and CH in Bu^i); 24.07 and 35.80 (C-3,5 and CH_2 in Bu^i); 49.03 (N^+—CH_3); 68.91 (C-2,6).

***cis*-2,6-Diisobutyl-1,1-dimethylpiperidinium iodide (15).** A mixture of compound **6** (0.28 g, 1.4 mmol), MeI (0.35 mL, 5.7 mmol), K_2CO_3 (0.39 g, 2.8 mmol), and ethanol (10 mL) was refluxed for 5 h. The reaction mixture was filtered. The solution was evaporated to dryness *in vacuo*. The residue was extracted with chloroform, filtered, and evaporated *in vacuo*. Crystallization from an ethyl acetate—EtOH mixture gave salt **15** (0.33 g, 66%), m.p. 148—149 °C. Found (%): C, 51.05; H, 9.12; I, 35.54. $C_{15}H_{32}NI$. Calculated (%): C, 50.99; H, 9.13; I, 35.92. ^{1}H NMR ($CDCl_3$), δ): 1.03 (d, 6 H, 2 CH_3); 1.08 (d, 6 H, 2 CH_3); 1.23—2.18 (w.m, 12 H, CH and CH_2); 2.86 (s, 3 H, N^+—CH_3); 3.35 (s, 3 H, N^+—CH_3); 4.08 (m, 2 H, C(2)—H and C(6)—H). ^{13}C NMR ($CDCl_3$), δ: 21.17 (C-4); 21.81, 23.50, 25.95 (CH_3 and CH in Bu^i); 27.17 and 38.96 (C-3,5 and CH_2 in Bu^i); 37.67 and 48.80 (N^+—CH_3); 72.55 (C-2,6).

***N*-(2′-Hydroxyethyl)-*cis*-2,6-diisobutylpiperidine (16)** was prepared analogously to **9** from compound **6** (1.78 g, 9.0 mmol), MeOH (4.5 mL), ethylene oxide (15% excess), and concentrated HCl (0.023 mL). The yield was 1.75 g (80%), b.p. 102—103 °C (1 Torr), $n_D^{13.5}$ = 1.4770. Found (%): C, 74.59; H, 12.71. $C_{15}H_{31}NO$. Calculated (%): C, 74.63; H, 12.94. IR (thin layer, ν/cm^{-1}): 1366, 1466, 2870, 2925, 2953 (CH_3, CH_2, CH); 1044, 3380 (br.) (C—OH). ^{1}H NMR ($CDCl_3$), δ: 0.86 (d, 6 H, 2 CH_3, ^3J = 6.6 Hz); 0.90 (d, 6 H, 2 CH_3, ^3J = 6.6 Hz); 1.05—1.85 (w.m, 12 H, CH and CH_2); 2.60 (t, 2 H, N—CH_2, ^3J = 6.1 Hz); 2.65 (2 H, C(2)—H and C(6)—H); 3.35 (br.s, 1 H, OH); 3.43 (t, 2 H, O—CH_2). ^{13}C NMR ($CDCl_3$), δ: 23.54 (C-4); 22.14, 23.71, 25.18 (CH_3 and CH in Bu^i); 26.19, 43.73, 45.45 (N—CH_2, C-3,5 and CH_2 in Bu^i); 60.54 (C-2,6); 60.73 (CH_2—OH).

***N*-(2′-Hydroxyethyl)-*trans*-2,6-diisobutylpiperidine (17)** was prepared analogously to **9** from compound **5** (1.92 g, 9.7 mmol), MeOH (5 mL), ethylene oxide (a 15% excess), and concentrated HCl (0.03 mL). The yield was 2.02 g (86%), b.p. 102—103 °C (1 Torr), n_D^{24} = 1.4677. Found (%): C, 74.79; H, 13.02. $C_{15}H_{31}NO$. Calculated (%): C, 74.63;

H, 12.94. IR (thin layer, ν/cm^{-1}): 1168, 1366, 1383, 1465, 2868, 2925, 2955 (CH_3, CH_2, CH); 1050, 3430 (br.) (C—OH). ^1H NMR ($CDCl_3$), δ: 0.8—1.0 (12 H, CH_3); 1.05—1.8 (w.m, 12 H, CH and CH_2); 2.5—2.95 (4 H, C(2)—H, C(6)—H, and N—CH_2); 3.3—3.65 (3 H, O—CH_2 and OH). ^{13}C NMR ($CDCl_3$), δ: 20.31 (C-4); 22.34, 22.82, 24.56 (CH_3 and CH in Bu^i); 24.90, 41.57, 46.20 (N—CH_2, C-3,5 and CH_2 in Bu^i); 51.81 (C-2,6); 58.47 (CH_2—OH).

***trans*-2,6-Dimetallyl-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridine (18).** Trimethallylborane (3.97 g, 22.5 mmol) was placed in a three-neck flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an inlet for argon. Deuteropyridine (3.61 mL, 45.1 mmol) was added. The temperature was maintained at not higher than 25 °C. Then 2-propanol (6.9 mL, 90.2 mmol) was added at 20 °C. The reaction mixture was stirred at ~20 °C. The low-boiling compounds were distilled off *in vacuo*. Triethanolamine (3 mL, 22.5 mmol) was added to the residue. Distillation gave compound **18** (3.63 g, 82%), b.p. 76—77 °C (2 Torr), $n_D^{19.5}$ = 1.4865. Found (%): C, 79.08; H, 8.17; D, 5.04. $C_{13}H_{16}D_5N$. Calculated (%): C, 79.52; H, 8.21; D, 5.09. IR (thin layer, ν/cm^{-1}): 894, 1375, 1444, 1645, 2070, 2155, 2270, 2920 (br.), 2970, 3075 (CH_2=C, R^1CD=CDR^2, CH_3, CH_2, CHD, and CDR); 3320 (NH). ^2H NMR ($CDCl_3$), δ: 1.58 (w.m, 1 D, CHD—C=); 2.60, 3.13 (m, 2 D, C(2)—D and C(6)—D); 5.32 (m, 2 D, CD=CD). ^1H NMR ($CDCl_3$), δ: 1.6—2.3 (12 H, CH_3, NH, CHD—C=, and CH_2—C=); 4.6—4.9 (m, 4 H, CH_2=C). ^{13}C NMR ($CDCl_3$), δ: 21.21, 21.39 (CH_3); 30.94 (t, C-3, $^1J_{^{13}C-^2H}$ = 19.1 Hz); 42.36, 43.95 (CH_2); 42.68 (t, $^1J_{^{13}C-^2H}$ = 20.1 Hz) and 48.57 (t, $^1J_{^{13}C-^2H}$ = 20.6 Hz) (C-2,6); 112.27 (=CH_2); 123.68 (t, $^1J_{^{13}C-^2H}$ = 24.1 Hz) and 128.52 (t, $^1J_{^{13}C-^2H}$ = 24.1 Hz) (C-4,5); 141.34, 141.76 (=C—).

Hydrochloride 18 · HCl was prepared from compound **18** (0.13 g, 0.7 mmol) and an ethereal solution of HCl in a yield of 0.14 g (91%), m.p. 192—193.5 °C (from an ether—methanol mixture). Found (%): C, 67.15; H, 7.46; D, 4.35; Cl, 15.06. $C_{13}H_{17}D_5NCl$. Calculated (%): C, 67.07; H, 7.36; D, 4.29; Cl, 15.23. ^2H NMR ($CDCl_3$), δ: 2.40 (w.m, 1 D, CHD—C=); 3.60, 3.80 (m, 2 D, C(2)—D and C(6)—D); 5.80 (m, 2 D, CD=CD). ^1H NMR ($CDCl_3$), δ: 1.78 (s, 3 H, CH_3); 1.81 (s, 3 H, CH_3); the AB-spectrum, δ_A = 2.44; δ_B = 2.92; J_{AB} = 13.2 Hz (4 H, CH_2—C=); 2.28 and 2.51 (s, the intensity ratio of *cis*- : *trans*- was ~1 : 1, 1 H, CHD—C=); 4.70—5.05 (m, 4 H, CH_2=C—); 9.40, 10.17 (both br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 22.05, 22.27 (CH_3); 25.49 (t, C-3, $^1J_{^{13}C-^2H}$ = 17.4 Hz); 39.05 and 39.11 (s, the intensity ratio of *cis*- : *trans*- CH_2 at C-2 was ~1 : 1), 40.73 (CH_2 in the other methallyl group); 47.3 (t, $^1J_{^{13}C-^2H}$ = 21.8 Hz) and 48.5 (t, $^1J_{^{13}C-^2H}$ = 21.0 Hz) (C-2,6); 114.79, 115.10 (=CH_2); 123.0 (t, $^1J_{^{13}C-^2H}$ = 23.3 Hz) and 124.2 (t, $^1J_{^{13}C-^2H}$ = 24.7 Hz) (C-4,5); 139.11, 139.40 (=C—).

1-Benzyl-*trans*-2,6-dimetallyl-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridine (19). A mixture of compound **18** (0.94 g, 4.8 mmol), benzyl chloride (0.55 mL, 4.8 mmol), K_2CO_3 (1.32 g, 9.6 mmol), and ethanol (10 mL) was refluxed for 5 h. Then ethanol was distilled off *in vacuo*. Water was added until the K_2CO_3 was completely dissolved. The reaction mixture was extracted with ether and dried with K_2CO_3. Distillation gave compound **19** (0.84 g, 61%), b.p. 121—122 °C (1 Torr), $n_D^{19.5}$ = 1.5273. Found (%): C, 83.45; H, 7.62; D, 3.47; N, 4.71. $C_{20}H_{22}D_5N$. Calculated (%): C, 83.85; H, 7.74; D, 3.49; N, 4.89. IR (thin layer, ν/cm^{-1}): 892, 1375, 1445, 1645, 2050, 2160, 2270, 2930 (shoulder), 2970, 3025, 3070 (CH_2=C—, R^1CD=CDR^2, CH_3, CH_2, CHD, and CDR); 1493, 1780, 1870, 1945 (Ph—). ^2H NMR ($CDCl_3$), δ: 2.13 (w.m, 1 D, CHD—C=); 3.35 (m, 2 D, C(2)—D and C(6)—D); 6.02 (m, 2 D, CD=CD). ^1H NMR ($CDCl_3$), δ: 1.42 (s, 3 H, CH_3); 1.77 (s, 3 H, CH_3); 1.88 (s, 1 H, CHD—C=); 2.0—2.4 (m, 4 H, CH_2—C=); AB-spectrum, δ_A = 3.41, δ_B = 3.75, J_{AB} = 13.7 Hz (2 H, CH_2Ph); 4.5—4.9 (m, 4 H, CH_2=C—). ^{13}C NMR ($CDCl_3$), δ: 22.09 (CH_3); 25.68 (t, C-3, $^1J_{^{13}C-^2H}$ = 18.9 Hz); 40.21 and 40.34 (s, the intensity ratio of *cis*- : *trans*- CH_2 at C-2 was ~1 : 1), 43.07 (CH_2 in the other methallyl group); 48.93 (t, $^1J_{^{13}C-^2H}$ = 20.3 Hz) and 54.62 (t, $^1J_{^{13}C-^2H}$ = 20.2 Hz) (C-2,6); 50.12 (N—C—Ph); 111.91, 112.00 (=CH_2); 124.40 (t, $^1J_{^{13}C-^2H}$ = 24.2 Hz) and 128.45 (t, $^1J_{^{13}C-^2H}$ = 24.2 Hz) (C-4,5); 143.00, 143.42 (=C—).; 126.34, 127.74, 128.70, 140.57 (Ph).

***N*-(2′-Heptafluoropropyl-2′-hydroxyethyl)-*trans*-2,6-dimethallyl-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridine (20).** A mixture of compound **18** (1.59 g, 8.1 mmol) and heptafluoropropylethylene oxide (1.75 g, 8.2 mmol) was heated at 120—130 °C for 2 h. Distillation gave a mixture of two diastereoisomers **20** (56 : 44) in a yield of 2.97 g (90%), b.p. 100—102 °C (1 Torr). According to the data of TLC (Al_2O_3), the mixture of diastereoisomers can be separated into components, but separation was not carried out. The spectra of two diastereoisomers are given below. ^1H NMR ($CDCl_3$), δ: 1.80 (s, 3 H, CH_3); 1.82 (s, 3 H, CH_3); 1.9—3.2 (w.m, 7 H, 2 CH_2—C=, CHD—C=, N—CH_2); 4.1 (m, 1 H, CH—CF_2); 4.45 (br.s, 1 H, OH); 4.85 (m, 4 H, CH_2=C—). ^{19}F NMR ($CDCl_3$), δ_{CFCl_3}: −80.76 (m, 3 F, CF_3); −126.6 (m, 2 F, CF_2—CF_3). The AB spectrum: δ_A = −124.2, δ_B = −129.0, J_{AB} = 282.8 Hz, and the AB spectrum: δ_A = −124.8, δ_B = −129.0, J_{AB} = 281.7 Hz (2 F, CF_2—CH(OH)).

***trans*-2,6-Dimethallyl-1,1-dimethyl-2,3,4,5,6-pentadeutero-1,2,3,6-tetrahydropyridinium iodide (21).** A mixture of compound **18** (0.51 g, 2.6 mmol), MeI (0.65 mL, 19.4 mmol), K_2CO_3 (0.72 g, 5.2 mmol), and ethanol (10 mL) was refluxed for 5 h. The solution was filtered and evaporated to dryness. The residue was extracted with chloroform, filtered, and evaporated *in vacuo*. Crystallization of the residue from an ethyl acetate—EtOH mixture gave salt **21** (0.78 g, 85%), m.p. 164—165 °C. Found (%): C, 51.08; H, 5.94; D, 2.81; I, 35.90. $C_{15}H_{21}D_5NI$. Calculated (%): C, 51.14; H, 6.01; D, 2.84; N, 3.99; I, 36.02. ^2H NMR ($CDCl_3$), δ: 2.24 (w.m, 1 D, CHD—C=); 3.91 (m, 2 D, C(2)—D and C(6)—D); 5.64 (m, 2 D, CD=CD). ^1H NMR ($CDCl_3$), δ: 1.89 (s, 3 H, CH_3); 1.90 (s, 3 H, CH_3). Two AB spectra: δ_A = 2.32, δ_B = 2.88, J_{AB} = 13.0 Hz, and δ_A = 2.32, δ_B = 2.96, J_{AB} = 13.0 Hz (4 H, CH_2—C=); 2.36 and 2.63 (s, the intensity *cis*- : *trans*- ratio was ~1 : 1, 1 H, CHD—C=); 3.40 (s, 3 H, N^+—CH_3); 3.58 (s, 3 H, N^+—CH_3); 4.8—5.1 (m, 4 H, CH_2=C—). ^{13}C NMR ($CDCl_3$), δ: 22.23, 22.32 (CH_3); 24.45 (t, C-3, $^1J_{^{13}C-^2H}$ = 17.4 Hz); 35.30, 36.04 (CH_2); 47.14, 49.19 (N^+—CH_3); 63.96 (t, $^1J_{^{13}C-^2H}$ = 18.8 Hz) and 65.13 (t, $^1J_{^{13}C-^2H}$ = 18.9 Hz) (C-2,6); 115.33, 115.72 (=CH_2); 121.59 (t, $^1J_{^{13}C-^2H}$ = 23.2 Hz) and 122.86 (t, $^1J_{^{13}C-^2H}$ = 24.7 Hz) (C-4,5); 137.70, 138.47 (=C—).

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