as to maintain constant pH. The mixture was kept for 24 h at 0 °C, and the pH value was maintained by the dropwise addition of a 20% aqueous solution of NaOH; then an additional 5 mL of 20% NaOH was added, and the mixture was kept for an additional 72 h at 20 °C in order to decompose the remaining chloramines. The yield of diaziridine was determined by iodometric titration of the mixture taking into account the results of blank entries.

To isolate 1,2-dimethyl- (**5a**), 1,2,3-trimethyl- (**5d**), 1,2-diethyl-3-methyldiaziridines (**5e**), 1,5-diazabicyclo[3.1.0]hexane (**5f**), and 6-methyl-1,5-diazabicyclo[3.1.0]hexane (**5g**), the reaction mixture was saturated with NaOH at 20—30 °C, and the upper layer was separated, dried with NaOH, and distilled three times.

To isolate 1,2-di(β-acetaminoethyl)diaziridine (**5b**) and 3-methyl-1,2-di(β-acetaminoethyl)diaziridine (**5c**), the reaction mixture was acidified at 0—5 °C with 50% H_2SO_4 to pH 7.0, half of the water was evaporated on a rotary evaporator, and the residue was diluted with a fivefold volume of MeOH. The mixture was kept for 30 min at 0 °C, the precipitate was filtered off, and the solvent was evaporated. The residue was dissolved in $CHCl_3$ and dried with K_2CO_3. Diaziridines were isolated on a column with silica gel L 40/100; elution was carried out with $CHCl_3$ washed twice with an equal volume of 25% aqueous NH_3.

Blank entries with RNHCl. An aqueous solution of NaOCl (0.05 mol) was added dropwise at 0 °C to a solution of an amine (0.1 mol) in 30 mL of H_2O. The mixture was kept for 24 h at 0 °C and for 72 h at -20 °C. The content of RNHCl was determined by iodometric titration (as a rule, it was 0—3% of the initial amount).

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Synthesis and molecular structure of *trans*-2,6-dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide

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The structure of *trans*-2,6-dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide was established by X-ray structural analysis. The corresponding base was synthesized by reductive diallylation of pyridine with trimethallylborane in the presence of 2-propanol.

Key words: allylboration, pyridine, trimethallylborane, *trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine, X-ray structural analysis.

Complexes of triallylborane with pyridine and its various derivatives are stable under an inert atmosphere but undergo complete rearrangement under the action of alcohols, water, or R_2NH to form the corresponding *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridines (in yields of 70—97%).[1—3] This stereospecific reaction occurs with "destruction of aromaticity" and is not complicated by

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[†] Deceased in 1995.

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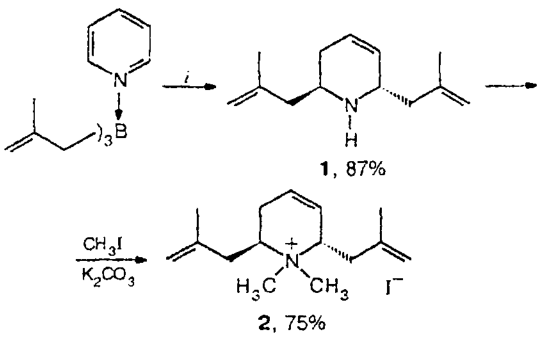
Table 1. Bond lengths (Å) in molecule **2**

Bond	*d*/Å	Bond	*d*/Å
N(1)—C(2)	1.532(6)	N(1)—C(6)	1.542(6)
N(1)—C(12)	1.508(7)	N(1)—C(13)	1.501(8)
C(1)—C(2)	1.537(8)	C(1)—C(10)	1.492(8)
C(2)—C(3)	1.494(8)	C(3)—C(4)	1.318(9)
C(4)—C(5)	1.489(9)	C(5)—C(6)	1.507(8)
C(6)—C(7)	1.532(7)	C(7)—C(8)	1.509(8)
C(8)—C(9)	1.317(8)	C(8)—C(15)	1.469(10)
C(10)—C(11)	1.330(9)	C(10)—C(14)	1.497(10)

side processes. The reaction is called reductive *trans*-2,6-diallylboration of pyridines with allylboranes. The structures of the piperideines formed were established by chemical and physicochemical methods, primarily by NMR spectroscopy.[2,3] The structures of *trans*-2,6-diallyl-3-bromo-Δ^3-piperideine hydrochloride[4] and *trans*-2-allyl-6-phenyl-Δ^3-piperideine hydrochloride[5] were established by X-ray structural analysis.

Recently, we have demonstrated that when treated with 2-propanol, the trimethallylborane—pyridine adduct (b.p. 75—77 °C (1 Torr), ^{11}B δ was −0.5) gave *trans*-2,6-dimethallyl-1,2,3,6-tetrahydropyridine (**1**) in a yield of 87%.[6]



1, 87%

2, 75%

i. 1. Pr^{i}OH (4 equiv.), 20 °C, 2 h
2. H_2O, OH^-

The reaction proceeds at room temperature and is completed in 2 h,[6] *i.e.*, the reaction conditions are milder than those in the case of triallylborane.[2,3] Hydrogenation of amine **1** yielded 2,6-diisobutylpiperidine, and a *trans* arrangement of its substituents was established by NMR spectroscopy (based on analysis of the spectrum of its *N*,*N*-dimethyl salt).[6] However, we would like to establish unambiguously the structure of **1**, particularly the mutual arrangement of the methallyl groups with respect to the ring. For this purpose, we obtained a single crystal of *N*,*N*-dimethyl salt **2** from amine **1** and studied it by X-ray structural analysis.

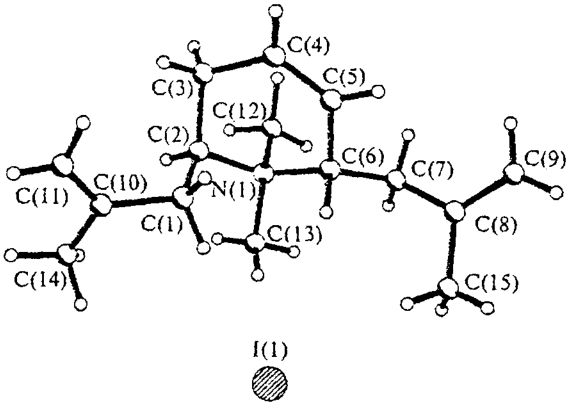


Fig. 1. Overall view of the molecule of *trans*-2,6-dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide **2**.

The overall view of molecule **2** is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2, respectively. The piperidine ring of the molecule has a half-chair conformation. The C(6) and N(1) atoms deviate from the mean plane (within ±0.003 Å) by 0.419 and −0.374 Å, respectively. The methallyl groups at the C(6) and C(2) atom are in axial and pseudo-equatorial positions, respectively. The bond lengths in the piperideine ring are close to those found previously in *trans*-2,6-diallyl-3-bromo-Δ^3-piperideine hydrochloride[4] and *trans*-2-allyl-6-phenyl-Δ^3-piperideine hydrochloride.[5] In the molecule, short intramolecular contacts occur between the iodide anion and the H(6) and H(122) atoms (I(1)···H(6) and I(1)···H(122) are 3.26(4) and 3.18(4) Å, respectively).

From the above-mentioned data it follows that the reaction of pyridine with trimethallylborane in the presence of alcohols occurs as stereospecific *trans*-addition of methallyl groups at positions 2 and 6 of the heterocycle.

Experimental

***trans*-2,6-Dimethallyl-1,2,3,6-tetrahydropyridine (1)** was synthesized by the reaction of trimethallylborane (7.17 g,

Table 2. Bond angles (ω) in molecule **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—N(1)—C(6)	109.4(3)	C(4)—C(5)—C(6)	110.4(5)	C(2)—N(1)—C(12)	110.3(4)	C(3)—C(4)—C(5)	123.2(6)
C(6)—N(1)—C(12)	108.8(4)	N(1)—C(6)—C(7)	112.8(4)	C(2)—N(1)—C(13)	110.2(4)	N(1)—C(6)—C(5)	110.2(4)
C(6)—N(1)—C(13)	109.7(4)	C(6)—C(7)—C(8)	111.2(4)	C(12)—N(1)—C(13)	108.3(4)	C(5)—C(6)—C(7)	110.4(4)
C(2)—C(1)—C(10)	111.4(4)	C(7)—C(8)—C(15)	116.3(6)	N(1)—C(2)—C(1)	113.7(4)	C(7)—C(8)—C(9)	121.4(6)
N(1)—C(2)—C(3)	109.6(4)	C(1)—C(10)—C(11)	121.3(6)	C(1)—C(2)—C(3)	111.5(4)	C(9)—C(8)—C(15)	122.3(6)
C(2)—C(3)—C(4)	125.5(6)	C(11)—C(10)—C(14)	122.2(7)			C(1)—C(10)—C(14)	116.4(5)

Table 3. Atomic coordinates (×10^4; for H, ×10^3) and equivalent isotropic temperature factors U_{cq} (×10^3/Å^2; for H, ×10^2/Å^2) for molecule **2**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
I(1)	2153(1)	9083(1)	1525(1)	68(1)
N(1)	2190(3)	5135(4)	3110(3)	45(1)
C(1)	1225(5)	2811(7)	3426(4)	54(2)
C(2)	2317(4)	3730(5)	3585(3)	45(2)
C(3)	3385(5)	3015(6)	3309(4)	58(2)
C(4)	4237(5)	3604(6)	2905(4)	61(2)
C(5)	4244(5)	5095(6)	2664(4)	55(2)
C(6)	3385(4)	5876(6)	3186(3)	45(2)
C(7)	3884(5)	6090(6)	4177(3)	51(2)
C(8)	4602(4)	7396(5)	4278(3)	51(2)
C(9)	5754(6)	7362(9)	4334(4)	65(2)
C(10)	1125(4)	1844(6)	4204(4)	53(2)
C(11)	1278(6)	492(8)	4110(7)	80(3)
C(12)	1782(6)	4951(8)	2115(4)	65(2)
C(13)	1305(5)	6002(8)	3540(5)	63(2)
C(14)	777(7)	2466(9)	5070(5)	74(3)
C(15)	3943(9)	8695(9)	4289(7)	93(3)
H(11)	61(4)	328(5)	336(3)	4(1)
H(12)	131(4)	229(6)	285(4)	6(2)
H(2)	240(3)	395(4)	426(3)	3(1)
H(3)	336(5)	209(6)	348(4)	7(2)
H(4)	490(5)	313(6)	277(4)	7(2)
H(51)	499(5)	549(5)	283(3)	6(2)
H(52)	408(5)	527(6)	200(4)	7(2)
H(6)	320(3)	670(4)	294(3)	2(1)
H(71)	319(5)	617(5)	456(4)	7(2)
H(72)	434(5)	533(6)	438(4)	6(2)
H(91)	621(5)	654(7)	423(4)	7(2)
H(92)	612(5)	812(6)	442(4)	6(2)
H(111)	160(5)	19(6)	355(4)	8(2)
H(112)	120(6)	−15(9)	458(5)	11(3)
H(121)	97(5)	462(6)	206(4)	6(2)
H(122)	180(6)	587(7)	184(5)	8(2)
H(123)	242(7)	436(8)	180(6)	13(3)
H(131)	54(5)	554(5)	343(3)	6(2)
H(132)	135(4)	679(6)	325(4)	6(2)
H(133)	156(6)	593(6)	424(5)	8(2)
H(141)	6(6)	290(6)	493(4)	8(2)
H(142)	127(7)	319(9)	534(5)	12(3)
H(143)	67(7)	186(9)	550(6)	12(3)
H(151)	351(5)	875(6)	482(4)	6(2)
H(152)	450(7)	954(9)	433(5)	12(3)
H(153)	327(9)	889(8)	388(7)	13(3)

40.74 mmol), pyridine (6.6 mL, 81.48 mmol), and 2-propanol (12.4 mL, 161.88 mmol) under an atmosphere of argon. The yield was 6.74 g (87%), b.p. 62—63 °C (1 Torr), n_D^{22} = 1.4880.[6]

***trans*-2,6-Dimethallyl-1,1-dimethyl-1,2,3,6-tetrahydropyridinium iodide (2)**[6]. A mixture of amine **1** (0.94 g, 4.91 mmol), MeI (1.24 mL, 19.64 mmol), and K_2CO_3 (1.38 g, 9.82 mmol) in ethanol (10 mL) was refluxed for 5 h. The reaction mixture was filtered, and the low-boiling compounds were distilled *in vacuo*. The product was extracted with chloroform. The extract was evaporated to dryness, and the residue was crystallized from an ethyl acetate—ethanol mixture. Salt **2** was isolated in a yield of 1.28 g (75%), m.p. 164—165 °C.

Single crystals of salt **2** were obtained by crystallization from an ethyl acetate—ethanol mixture. The crystals are monoclinic, M = 347.3 [$C_{15}H_{26}NI$], space group $P2_1/C$, Z = 4, at 23 °C: a = 11.465(2) Å, b = 9.691(4) Å, c = 14.722(4) Å, β = 95.11(3)°, V = 1629.2(6) Å^3, d_{calc} = 1.416 g cm^{-3}. The unit cell parameters and intensities of 2084 independent reflections with $I \geq 2\sigma(I)$ were measured on an Enraf-Nonius Cad-4 diffractometer (λ-Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, 2θ ≤ 54°). The structure of salt **2** was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. All hydrogen atoms were revealed from the difference Fourier synthesis and refined isotropically. The final values of the R factors were as follows: R = 0.038 and R_w = 0.042. All calculations were carried out on an IBM-PC/AT computer using the SHELXTL PLUS program package.[7] The atomic coordinates and thermal parameters of the structure of **2** are given in Table 3.

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