

ON HYDROBORATION OF 5-DIMETHYLAMINO-3-METHYL-1-PENTENE AND 5-DIMETHYLAMINO-3,3-DIMETHYL-1-PENTENE*

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Hydroboration of 5-dimethylamino-3-methyl-1-pentene and 5-dimethylamino-3,3-dimethyl-1-pentene as well as the thermal transformation of 5-dimethylamino-3-methyl-1-pentene-borane and 5-dimethylamino-3,3-dimethyl-1-pentene-borane were investigated. The six- or seven-membered ring derivatives formed were hydrolysed and oxidized to secondary or primary amino alcohols, respectively.

In the preceding papers of this series hydroboration of some ω -dimethylamino-alkenes¹⁻⁴ has been described. During hydroboration at elevated temperature isomerization of primarily formed products took place, so that after oxidation with hydrogen peroxide in alkaline medium amino alcohols were isolated which corresponded to the oxidation of cyclic amine-boranes with a five-membered, six-membered and seven-membered ring. The aim of this work was to investigate the hydroboration of 5-dimethylamino-3,3-dimethyl-1-pentene (*Ib*) as well as 5-dimethylamino-3-methyl-1-pentene (*Ia*). In the case of the first mentioned compound the methyl groups bound to the carbon atom No 3 prevent a shift of the double bond. For this reason we expected amine-boranes with a six-membered and a seven-membered ring only as the products of hydroboration.

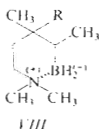
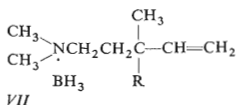
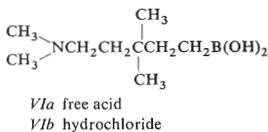
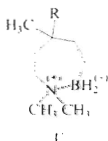
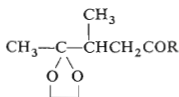
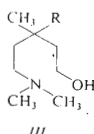
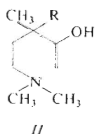
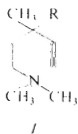
On hydroboration of *Ib*, carried out with diborane prepared directly in the reaction mixture, and followed by oxidation with hydrogen peroxide in alkaline medium a mixture of two amino alcohols was obtained in an approximately 4 : 1 ratio. These alcohols were isolated in pure form and identified on the basis of analyses and NMR spectra as *IIIb* and *IIB*. A similar ratio of products was also obtained by hydroboration of *Ib* with triethylamine-borane in toluene at 140–145°C and subsequent oxidation.

Hydroborations of *Ia* carried out in the same manner afforded a mixture of two amino alcohols, *IIIa* and *IIa*. In contrast to both hydroborations of amine *Ib*, when the ratio of amino alcohols *IIIb* and *IIB* is almost the same after hydroboration

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carried out in the cold or under heating, the hydroboration of amine *Ia* gave appreciably different results in dependence on the working conditions. On hydroboration of amine *Ia* under heating almost a double amount of secondary amino alcohol *Iia* was formed in comparison with the reaction carried out in the cold (to the detriment of the primary amino alcohol *Iiaa*). As in this case only the primary amino alcohol *Iiaa* could be isolated in pure form, we prepared the secondary amino alcohol *Iia* synthetically. The starting ethyl ester of β -methyllevulinic acid⁵ was converted to ethylene acetal *IVa* from which we prepared dimethylamide of β -methyllevulinic acid ethylene acetal (*IVb*) on reaction with dimethylaminomagnesiyl iodide⁶. Hydrolysis of *IVb* gave dimethylamide of β -methyllevulinic acid which was reduced with lithium aluminum hydride to 3-methyl-5-dimethylamino-2-pentanol (*Iia*), identical with the minor product of hydroboration and subsequent oxidation of the unsaturated amine *Ia*. The results of these hydroborations are summarized in Table I.

In the subsequent phase of our work we tried to isolate the primary products of hydroboration of both unsaturated amines *Ia* and *Ib*. We carried out the hydroboration of triethylamine-borane under heating and endeavoured to isolate the product by distillation in a vacuum. It was observed, similarly as in our earlier studies¹⁻⁴, that the product distills only at a bath temperature which is much above



R for *I-III*, *V*, *VII*, *VIII*:
a = H, b = CH₃

its boiling point. This is evidently due to thermal decomposition of the substance which is probably polymeric. The product obtained was in both cases separated to three fractions and a part of each was hydrolysed with hydrochloric acid and oxidized with hydrogen peroxide in alkaline medium. As it was observed that the product of these conversions of the highest boiling fraction was individual and that it corresponded to amino alcohols *IIIa* or *IIIb*, the residue of the highest boiling fraction from the hydroborations of amines *Ia*, *Ib* was submitted to analysis and its NMR spectrum was measured.

The PMR spectra of compounds containing boron after hydroboration of unsaturated amines *I* and isolation of the main product are very similar. The C-methyl group signals lie in the 0.9 p.p.m. region. The signals of N-methyl group protons are shifted approximately by 0.3 p.p.m. downfield in comparison with the compounds having a free dimethylamino group, *IIa*, *IIb* and *IIIa*, *IIIb*, *i.e.* to a region where the signals of analogous protons of amine-boranes *VIIa* and *VIIb* may be found. The signal of the N—CH₃ groups in compound *Va* is also split into two singlets at 37°C. This shift indicates that an intramolecular bond was formed between the dimethylamino group nitrogen and the boron atom giving rise to a cyclic structure. A striking character of the spectra of compounds *Va*, *Vb* is further the presence of a broad, badly resolved band (in the proximity of the tetramethylsilane signal), corresponding to two protons. On decoupling of ¹¹B this signal is far better resolved, but it in no way changes its position and the signal of B—H protons appears as a broad band at 1.7–1.9 p.p.m. On hydrolysis of *Vb* with dilute hydrochloric acid the hydrochloride of aminoboronic acid was obtained from which the acid *VI* was set free. In the NMR spectra of both these compounds analogous peaks appear between 0.5 and 0.9 p.p.m. According to decoupling results they may be assigned to the CH₂ group on the boron atom in the structure *VIa* and *VIb*. On the basis of these facts the band at high field in compounds *Va* and *Vb* may be explained similarly to the signal of the methylene group on boron and the whole spectrum assigned to structure *V*. In both cases the spectra do not permit the exclusion of a small admixture of compound *VIII* with a six-membered ring and boron bound to a secondary carbon atom. Hydrolysis of compounds *Va* and *Vb* with dilute hydrochloric acid and subsequent oxidation of the hydrochlorides of aminoboronic acids thus formed gave amino alcohols *IIIa* and *IIIb* exclusively. During hydroboration carried out without the separation of amine-boranes by distillation a mixture of amino alcohols *IIa*, *IIIa*, or *IIb*, *IIIb* was obtained after hydrolysis and oxidation, that corresponded to a true ratio of addition of diborane to both carbon atoms of the double bond, and in which the primary alcohol always predominated (Table I).

Finally we were also interested in the thermal conversion of amine-boranes *VII*. These substances were obtained similarly as in our preceding studies¹⁻⁴ from hydrochlorides of unsaturated amines *Ia*, *Ib*, under the effect of sodium borohydride. The products obtained can be distilled and according to NMR spectra they have the

acyclic structure of amine-boranes with a terminal double bond *VIIa* and *VIIb*. On heating of both these substances at 222–225°C pure products are formed to which the structures with a six-membered ring, *VIIIa* and *VIIIb* may be assigned on the basis of analytical evidence. On acid hydrolysis and subsequent oxidation in alkaline medium secondary amino alcohols *IIa* and *IIb* were obtained exclusively, and therefore we consider the six-membered ring as proved.

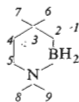
TABLE I

Results of Hydroborations of Unsaturated Amines, after Hydrolysis and Oxidation

Unsaturated amine	Temperature °C	Yield %	Amino alcohol	
			<i>II</i> , %	<i>III</i> , %
<i>Ia</i>	25	31	32	68
<i>Ia</i>	145	61	17	83
<i>Ib</i>	25	41	19	81
<i>Ib</i>	145	76	18	82

TABLE II

¹³C - NMR Spectra of *VIIIa* (a mixture of *cis* and *trans* isomers) and *VIIIb* in Hexadeuterioacetone (in p.p.m. in the direction of lower field with respect to TMS)



Atom	<i>VIIIa - cis</i>	<i>VIIIa - trans</i>	<i>VIIIb</i>
1	16.5	16.5	12.5
2	18 – 30 ^a		25.5 – 30 ^a
3	32.5	38.8	32.3
4	30.5	32.5	38.7
5	57.0	61.7	57.8
6	13.3	20.0	19.1
7	—	—	30.6
8-9	46.2 and 53.6	47.7 and 54.2	46.4 and 54.1

^a Very broad.

The results of NMR measurements after thermal conversion of acyclic amineboranes *VIIa* and *VIIb* when compared with the results obtained with the compounds prepared by normal hydroboration procedure (*Va*, *Vb*) indicate a distinct change in the character of the PMR spectra. The N-methyl group signals again form two singlets in the 2.55 p.p.m. region, which indicates a cyclic structure and the coordination of the boron atom to the free electron pair on nitrogen. The geminal methyl groups in compound *VIIIb* afford two singlets at 0.85 and 0.96 p.p.m., the analogous methyl group in compound *VIIIa* gives two superimposed doublets in the same region. In the spectra of both compounds a broad unresolved band at 0.6–0.9 p.p.m. may be found which according to the integration curve corresponds to three protons. At decoupling of the isotope ^{11}B this band is changed approximately to a singlet, or in the case of compound *VIIIa*, to two singlets with somewhat differing intensities. Gradual hydrolysis of compounds *VIIIa* and *VIIIb* causes these peaks to disappear at high fields and to increase the methyl group peaks at 0.9 p.p.m..

^{11}B NMR spectrum of compound *VIIIb* gives a triplet of boron at 28.5 p.p.m. shifted upfield in comparison with boric acid trimethyl ester (as external standard), with a coupling constant $^1J_{\text{B-H}} = 96$ Hz. The ^{13}C NMR spectra of compounds *VIIIa* and *VIIIb* were measured in hexadeuterioacetone and hexadeuteriobenzene both by noise-decoupling and by off-resonance decoupling of protons. For the assignment of single signals the comparison with the spectrum of triethylamine-borane (in hexadeuterioacetone $\delta_{\text{CH}_3}^{\text{TMS}} = 8.2$; $\delta_{\text{CH}_2}^{\text{TMS}} = 52.2$ p.p.m.) and with the data on the effect of the substitution on the chemical shift values⁷⁻¹⁰ was also made use of. It was found that compound *VIIIb* was pure, while compound *VIIIa*, giving after hydrolysis and oxidation a mixture of amino alcohols of *threo* and *erythro* configuration *IIa*, was a mixture of two stereoisomers. The results of ^{13}C NMR experiments summarized in Table II, as well as the PMR and ^{11}B NMR spectra¹¹ are in agreement with the structure *VIII* in which the nitrogen atom forms a dative bond with the boron atom, under formation of a six-membered ring. The number of signals in the ^{13}C NMR spectrum of *VIIIa* may be explained by the supposition that the methyl group on carbon atom 3 is equatorial in both configurations. Moreover this supposition is understandable — in the *trans* isomer three methyls would otherwise be in axial positions, in the *cis* isomer only two, but in the positions 1,3. The methyl group on carbon 3 is the sole carbon atom in the molecule which gives the same signal in both isomers of compound *VIIIa*. The determination of the shift of carbon 3 is hampered by a great error — its signal is strikingly broadened under the effect of the quadrupole moment of boron and it is detectable only with great difficulty. The fact remains unexplained that the proton signals of methyl groups in the β -position to the boron atom afford a very badly resolved and broad signal in spite of the appreciable distance from boron. It is possible that this fact is given by the effect of the quadrupole moment of boron atom *via* the bonding electrons.

In hydroboration in the cold compound *Ia* gives after hydrolysis and oxidation

32% of secondary alcohol *Ila*. In hydroboration of *Ia* under heating and in hydroboration of *Ib* (without regard to the working conditions) only about 18% of secondary alcohol *Ila* or *Ilb* are always formed. From this it may be judged that the six-membered ring *VIII* is formed relatively most easily at a lower temperature, and that for the addition of boron to carbon 2 the steric hindrance in the position 3 is decisive, which in compound *Ib* decreases — in comparison with compound *Ia* — the proportion of the product with a six-membered ring *VIII*. Different results are obtained on thermal conversion of acyclic amine-boranes *VII*, during which a structure with a six-membered ring and with the boron atom bound with the nitrogen by a dative bond, *VIII*, is formed exclusively. On hydrolysis and subsequent oxidation secondary alcohols *Ila* and *Ilb* are formed. It is probable that the mechanism of this thermal conversion is different from the mechanism of hydroboration proper.

EXPERIMENTAL

All hydroboration experiments and operations with the boron compounds were carried out under nitrogen. Gas chromatography was carried out on a Chrom II apparatus (column length 170 cm, diameter 0.6 cm, 20% of Tridox on porovina, carrier gas nitrogen). The NMR spectra were measured with an XL-100-15 instrument, ^1H at 100.1 MHz, ^{11}B at 32.1 MHz, and ^{13}C at 25.2 MHz in deuteriochloroform, hexadeuterioacetone or hexadeuteriobenzene; the working temperature was 37°C. The assignment was carried out both on the basis of chemical shifts and the multiplicity of signals, and according to the results of multiple resonance. The mass spectra were measured on a Gas Chromatograph-Mass Spectrometer LKB 9000 Produkter AB, Stockholm. Some samples were introduced *via* the gas chromatography column (length 2.5 m, 20% of Carbowax 20M on Chromosorb W, carrier gas helium). The temperature data are uncorrected.

Hydroboration of 5-Dimethylamino-3-methyl-1-pentene (*Ia*)

A) *Under heating*: A mixture of 6.65 g of *Ia* (ref.¹²) and 6.05 g of triethylamine-borane in 80 ml of toluene was refluxed at 140–145°C (bath temperature) for 6 hours. The solvent and triethylamine were distilled off through a column (bath temperature up to 155°C). The yield of the crude product was 7.1 g (97%). Its solution in 100 ml of acetone was refluxed with 31 ml of 4.9M hydrochloric acid for 20 minutes, the solvents were evaporated and the residual hydrochlorides (10.53 g; 98%) were suspended in 76.5 ml of tetrahydrofuran and alkalized with 26.5 ml of 40% sodium hydroxide solution. Hydrogen peroxide (30%, 26.5 ml) was added dropwise to the stirred solution over 10 minutes and the mixture was boiled for 5 hours. The aqueous layer was extracted with chloroform and the combined extracts were dried over potassium carbonate. Conventional isolation procedure afforded 4.44 g (61%) of a product, b.p. 107–111°C/10 Torr, containing 83% of 5-dimethylamino-3-methyl-1-pentanol (*IIIa*) and 17% of 5-dimethylamino-3-methyl-2-pentanol (*IIa*). The latter was determined on the basis of comparison with a synthetic sample. Redistillation gave pure 5-dimethylamino-3-methyl-1-pentanol, b.p. 109–111°C/10 Torr. For $\text{C}_8\text{H}_{19}\text{NO}$ (145.25) calculated: 66.16% C, 13.19% H, 9.64% N; found: 66.46% C, 13.12% H, 9.61% N. NMR spectrum (p.p.m.): $\text{CH}_3\text{—C}$ 0.9 (d; 6.5 Hz); CH_2CHCH_2 1.1–1.7 (m); $(\text{CH}_3)_2\text{N}$ 2.22 (s); CH_2N 2.0 to 2.6 (m); CH_2O 3.62 (t; 7 Hz).

B) *In the cold*: Compound *Ia* (6.35 g) and boron trifluoride etherate (15.8 g) dissolved in 25 ml of diglyme were added to a solution of 3.15 g of sodium borohydride in 75 ml of diglyme at

25–26°C over 2 hours. The mixture was stirred for two hours, decomposed with 5.5 ml of water and 26 ml of 36% hydrochloric acid, alkalinized with 42.5 ml of 40% sodium hydroxide solution, and eventually added dropwise with 35 ml of 30% hydrogen peroxide. After 3 hours' stirring the diglyme layer was separated and the aqueous layer extracted with chloroform. The extracts were combined with the diglyme layer, acidified with ethereal hydrogen chloride solution and evaporated. The residue was dissolved in 25 ml of water, the solution extracted with chloroform, alkalinized with a 40% sodium hydroxide solution, extracted with chloroform and the extract dried over potassium carbonate. Distillation gave 1.7 g (31%) of a mixture containing 68% of *IIIa* and 32% of *IIa* (b.p. 105°C/15 Torr).

Hydroboration of 5-Dimethylamino-3,3-dimethyl-1-pentene (*Ib*)

A) *Under heating*: A mixture of 7.4 g of *Ib* (ref.¹³) and 6.05 g of triethylamine-borane in 80 ml of toluene was refluxed for 6 hours (bath temperature 140–145°C). The working up of the reaction gave, as in the first case, a mixture of products, b.p. 106–112°/10 Torr; it weighed 6.37 g (76%) and consisted of 82% of 5-dimethylamino-3,3-dimethyl-pentanol (*IIIb*) and 18% of 5-dimethylamino-3,3-dimethyl-2-pentanol (*IIb*). Redistillation gave pure *IIIb*, b.p. 109–112°C/10 Torr. For C₉H₂₁NO (159.3) calculated: 67.87% C, 13.29% H, 8.79% N; found: 68.02% C, 13.31% H, 8.82% N. NMR spectrum (p.p.m.): (CH₃)₂C 0.92 (s); CH₂—C—CH₂ 1.31–1.61 (m); (CH₃)₂N 2.23 (s); CH₂N 2.29 (t; 6.5 Hz); CH₂O 3.63 (t; 7 Hz).

B) *In the cold*: Compound *Ib* (7.05 g) and 15.8 g of boron trifluoride etherate dissolved in 25 ml of diglyme were added over 3 hours to a solution of 3.15 g of sodium borohydride in 75 ml of diglyme at 25–26°C. Working up as in the preceding case gave 3.39 g (41%) of a mixture, b.p. 105–107°C/10 Torr, containing 81% of *IIIb* and 19% of *IIb*. From this mixture pure *IIb* was isolated by fractional distillation, b.p. 93–95°C/10 Torr. For C₉H₂₁NO (159.3) calculated: 67.87% C, 13.29% H, 8.79% N; found: 67.81% C, 13.37% H, 8.75% N. NMR spectrum (p.p.m.): (CH₃)₂C 0.86 (s) and 0.88 (s); CH₃—C—O 1.09 (d; 7 Hz); C—CH₂—C 1.45 (m); (CH₃)₂N 2.25 (s); CH₂N 2.31 (t; 7 Hz); CH—O 3.40 (q; 7 Hz).

Ethyl Ester of β-Methyllevulinic Acid Ethylene Acetal (*IVa*)

A mixture of 10.2 g of ethyl ester of β-methyllevulinic acid⁵, 8.1 g of ethylene glycol, and a solution of 70 mg of *p*-toluenesulfonic acid in 67 ml of benzene was refluxed in an apparatus with an azeotropic mixture separator for 6 hours. The mixture was washed with 1% sodium hydrogen carbonate solution and the benzene solution was dried over magnesium sulfate and distilled, b.p. 123–126°C/19 Torr, yield 7.7 g (60%). For C₁₀H₁₈O₄ (202.25) calculated: 59.39% C, 8.97% H; found: 59.47% C, 9.00% H.

Dimethylamide of β-Methyllevulinic Acid Ethylene Acetal (*IVb*)

Dimethylamine (3.75 g) in 66 ml of diethyl ether was added to a solution of methylmagnesium iodide (from 1.18 g of magnesium, 6.8 g of methyl iodide, and 30 ml of diethyl ether) dropwise and under stirring at a temperature below 0°C. The mixture was stirred under cooling for 3 hours⁶, a solution of 3.2 g of ethyl ester of β-methyllevulinic acid ethylene acetal in 30 ml of diethyl ether was added (the reaction was carried out under nitrogen), and the mixture was refluxed for 4 hours. A solution of 15.4 g of ammonium chloride in 47 ml of water was then added dropwise to the mixture which was extracted with diethyl ether and the extract washed with saturated sodium chloride solution and dried over magnesium sulfate. After evaporation of the solvent the residue was

mixed with 16 ml of methanol and 4.4 ml of 2M-NaOH and allowed to stand for 30 minutes. A saturated sodium chloride solution (88 ml) was then added and the mixture extracted with diethyl ether. The extract was washed with 1M-Na₂CO₃, then with a saturated sodium chloride solution, dried over sodium sulfate and worked up in the usual manner. Yield 0.98 g (31%) of a product boiling at 100–101°C/1 Torr. For C₁₀H₁₉NO₃ (201.3) calculated: 59.68% C, 9.52% H; found: 59.43% C, 9.67% H. NMR spectrum (p.p.m.): CH₃C<_C 1.01 (d; 7 Hz); CH₃C<_O 1.26 (s); CH₂—CH 1.84–2.90 (m); CH₃N 2.96 (s) and 3.04 (s); CH₂O 3.95 (s).

Dimethylamide of β-Methyllevulinic Acid

A mixture of 2.73 g of dimethylamide of β-methyllevulinic acid ethylene acetal and 20 ml of 3% hydrochloric acid was stirred for 6 hours, then extracted with chloroform and worked up in the conventional manner, to afford 1.6 g (75%) of product, b.p. 132–133°C/16 Torr. For C₈H₁₅NO₂ (157.2) calculated: 61.12% C, 9.62% H, 8.91% N; found: 61.11% C, 9.68% H, 8.95% N. NMR spectrum (p.p.m.): CH₃C<_C 1.13 (d; 7 Hz); CH₃CO 2.25 (s); CH₂ 2.10–2.43 (m); CH 2.85 to 3.30 (m); CH₃N 2.91 (s) and 3.02 (s).

5-Dimethylamino-3-methyl-2-pentanol (IIa)

A solution of β-methyllevulinic acid dimethylamide (1.47 g) in 30 ml of diethyl ether was added dropwise to a suspension of 1 g of lithium aluminum hydride in 100 ml of diethyl ether and the mixture was refluxed for 8 hours. After decomposition with 1 ml of water, 1 ml of 15% sodium hydroxide solution and 3 ml of water the precipitate was filtered off and the ethereal solution dried over potassium carbonate. Ether was evaporated and the residue distilled, b.p. 90.5–92.5°C/14 Torr, yield 0.85 g (63%). For C₈H₁₉NO (145.25) calculated: 66.16% C, 13.19% H, 9.64% N; found: 66.19% C, 13.26% H, 9.75% N. The substance is identical with the minor product of hydroboration of compound *Ia*. On the basis of gas chromatography two stereoisomers were identified which are formed in a 19 : 1 ratio and which have identical mass spectra. NMR spectrum (p.p.m.): CH₃C—O 1.12 (d; 6.5 Hz) and 1.15 (d; 6.5 Hz); CH₃C<_C 0.90 (d; 7 Hz); (CH₃)₂N 2.25 (s); CH₂N 2.05–2.58 (m); CCH₂CH 1.25–1.80 (m); CH—O 3.43 (m) and 3.73 (m).

1,1,5-Trimethyl-1-aza-2-boracycloheptane (Va)

A mixture of 6.65 g of *Ia* (ref.¹²) and 6 g of triethylamine-borane in 80 ml of toluene was refluxed for 6 hours (bath temperature was 140–145°C). Triethylamine and toluene were distilled off through a column and the residue distilled from a bath 205–220°C hot. Yield 4.2 g (58%), b.p. 94°C/2.2 Torr. For C₈H₂₀BN (141.1) calculated: 68.11% C, 14.29% H, 7.67% B, 9.93% N; found: 68.35% C, 14.33% H, 7.80% B, 9.87% N. NMR spectrum (p.p.m.): CH₃C 0.91 (d; 6 Hz); CH₂—B 0.20–0.70 (very broad); CH₃N 2.53 (s) and 2.56 (s); CH₂N 2.70–2.90 (m); other CH 1.1–2.1.

1,1,5,5-Tetramethyl-1-aza-2-boracycloheptane (Vb)

From 7.4 g of *Ib* (ref.¹³) and 6.1 g of triethylamine-borane 5.1 g (63%) of *Vb* were obtained in a similar manner, b.p. 119°C/2.2 Torr (bath temperature 220–250°C), m.p. 74–75°C. For

$C_9H_{22}BN$ (155.1) calculated: 69.69% C, 14.30% H, 6.98% B, 9.03% N; found: 69.48% C, 14.28% H, 6.84% B, 8.87% N. NMR spectrum (p.p.m.): $(CH_3)_2C$ 0.91 (s); CH_2B 0.20—0.55 (very broad); CH_3N 2.55 (s); CH_2N 2.65—2.85 (m); other CH 1.2—1.8.

Hydrochloride of 3,3,5,5-Tetramethyl-5-aminopentane-1-boronic Acid (*Vib*)

A solution of 1.7 g of compound *Vb* in 21 ml of acetone and 6 ml of 4.9M hydrochloric acid was refluxed for 20 minutes and evaporated. The residue (2.42 g; 98%) was hygroscopic, m.p. 102.5—104°C (2-propanol). For $C_9H_{23}BClNO_2$ (223.6) calculated: 48.35% C, 10.37% H, 15.86% Cl; found: 48.26% C, 10.49% H, 16.02% Cl. NMR spectrum (p.p.m.): $(CH_3)_2C$ 0.90 (s); CH_2B 0.50—0.85 (broad); CH_2-C-B 1.25—1.50 (m); CH_2 $\begin{matrix} C \\ \diagup \\ C \end{matrix}$ 1.65—1.90 (m); $(CH_3)_2N$ 2.82 (s); CH_2N 3.0—3.25 (m) (in hexadeuterioacetone).

5-Dimethylamino-3,3-dimethyl-1-pentene-borane (*VIIb*)

Hydrochloride of compound *Ib* (5.4 g) of m.p. 204°C (ethanol) was suspended in 30 ml of diethyl ether and 1.72 g of sodium borohydride were added to it under cooling and stirring. The suspension was stirred for one hour, additioned with 3.6 ml of water and stirred again for another 40 minutes. The ethereal layer was separated and the aqueous layer extracted with light petroleum and the extracts dried with potassium carbonate. After filtration of the solvents compound *VIIb* was obtained, b.p. 77°C/1 Torr, or 80.5°C/1.5 Torr, m.p. 31—31.5°C, yield 3.07 g (65%). For $C_9H_{22}BN$ (155.1) calculated: 69.69% C, 14.30% H, 9.03% N; found: 69.75% C, 14.53% H, 9.06% N. NMR spectrum (p.p.m.): $(CH_3)_2C$ 1.04 (s); CH_2 $\begin{matrix} C \\ \diagup \\ C \end{matrix}$ 1.58—1.81 (m); $(CH_3)_2N$ 2.55 (s); CH_2N 2.58—2.8 (m); $CH_2=$ 4.82—5.08 (m); $CH=$ 5.56—5.91 (m).

Thermal Conversion of 5-Dimethylamino-3,3-dimethyl-1-pentene-borane (*VIIb*)

Amine-borane *VIIb* was heated at 225°C for 2 hours and distilled, b.p. 72.5—73°C/0.9 Torr, or 75°C/1 Torr. Mass spectrum: $(M)^+ = 155$. For $C_9H_{22}BN$ (155.1) calculated: 69.29% C, 14.32% H, 6.98% B, 9.24% N; found: 69.41% C, 14.31% H, 6.90% B, 8.95% N. NMR spectrum indicates the structure of 1,1,3,4,4-pentamethyl-1-aza-2-boracyclohexane (*VIIIb*): CH_3-C-B 0.55—0.75 (broad); CH_3-C-CH_3 0.85 (s) and 0.96 (s); $CH-B$ 0.8—1.1 (broad); $C-CH_2-C$ 1.1—1.8 (m); CH_3N 2.54 (s) and 2.57 (s); CH_2N 2.3—3.1 (m) p.p.m.

Hydrolysis and oxidation: Hydrochloric acid (13 ml; 4.9M) was added to a solution of 3.15 g of substance *VIIIb* in 35 ml of acetone and the mixture refluxed for 20 minutes. After evaporation of the solution 3.8 g (83%) of product were obtained which was dissolved in 12 ml of tetrahydrofuran, mixed with 12 ml of 40% sodium hydroxide solution and dropwise addition of 12 ml of 30% hydrogen peroxide, and refluxed under stirring for 5 hours. The separated aqueous layer was extracted with light petroleum. The combined organic extracts were dried over potassium carbonate, the solvents evaporated and the residue distilled, b.p. 95—98°C/13 Torr, 1.25 g (47%). For $C_9H_{21}NO$ (159.3) calculated: 67.87% C, 13.29% H, 8.79% N; found: 67.81% C, 13.40% H, 8.86% N. NMR spectrum and elution data indicated that the product consisted of *IIB* as the sole component.

5-Dimethylamino-3-methyl-1-pentene-borane (*VIIa*)

Sodium borohydride (3.2 g) was added under cooling to a suspension of hydrochloride *Ia* (9.7 g) in 25 ml of diethyl ether and the mixture stirred for one hour. Water (6.6 ml) was then added and the stirring continued for another 40 minutes. The working up of the reaction mixture as in the first case gave 4.3 g (52%) of *VIIa*, b.p. 67°C/0.7 Torr. For $C_8H_{20}BN$ (141.1) calculated: 68.11% C, 14.29% H, 7.67% B, 9.93% N; found: 68.14% C, 14.60% H, 7.80% B, 10.02% N. NMR spectrum (p.p.m.): CH_3C 1.06 (d; 6.5 Hz); CH_2 $\left\langle \begin{array}{l} C \\ C \end{array} \right\rangle$ 1.4–1.9 (m); CH 1.9–2.30 (m); $(CH_3)_2N$ 2.55 (s); CH_2N 2.40–2.95 (m); $CH_2=$ 4.9–5.1 (m); $CH=$ 5.26–5.87 (m).

Thermal Conversion of 5-Dimethylamino-3-methyl-1-pentene-borane (*VIIa*)

Amine-borane *VIIa* was heated at 222°C for 2 hours and then distilled, b.p. 57–58°C/1 Torr. Mass spectrum: $(M)^+ = 141$. For $C_8H_{20}BN$ (141.1) calculated: 68.11% C, 14.29% H, 7.67% B, 9.93% N; found: 68.46% C, 14.37% H, 7.64% B, 9.83% N. NMR spectrum is identical with 1,1,3,4-tetramethyl-1-aza-2-boracyclohexane (*VIIIA*): CH_3C-B 0.65–0.90 (broad); CH_3C-CH 0.85–1.05 (m); $CH-B$ 0.8–1.2 (broad); CH_3N 2.53 (s) and 2.56 (s); CH_2N 2.50–3.05 (m); other peaks 1.2–2.1 p.p.m. (mixture of *cis* and *trans* isomers).

Hydrolysis and oxidation: A mixture (0.75 g) of the products of thermal conversion of *VIIa* in 10 ml of acetone was refluxed with 2.48 ml of 6.28M hydrochloric acid for 20 minutes. After evaporation 1.0 g (90%) of the product were obtained; tetrahydrofuran (4 ml) was added to the residue, followed by 4 ml of 40% sodium hydroxide solution and 4 ml of 30% hydrogen peroxide and the stirring and refluxing continued for 5 hours. After the conventional working up a product boiling at 86°C/10 Torr was obtained. Comparison of its elution times with those of standards demonstrated that the substance is identical with *IIa*. For $C_8H_{19}NO$ (145.25) calculated: 66.16% C, 13.19% H, 9.64% N; found: 66.53% C, 13.16% H, 9.68% N.

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