

HYDROBORATION OF N,N-DIMETHYL(2-VINYLBENZYL)AMINE*

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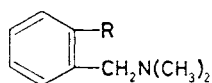
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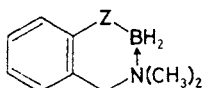
Hydroboration of N,N-dimethyl(2-vinylbenzyl)amine followed by oxidation afforded a mixture of primary and secondary alcohol, *i.e.* 2-(2-dimethylaminomethylphenyl)ethanol and 1-(2-dimethylaminomethylphenyl)ethanol, together with the reduction product — 2-ethyl(N,N-dimethylbenzylamine).

Styrene and its derivatives substituted on the benzene ring have been hydroborated with various reagents such as sodium borohydride and boron trifluoride diethyl etherate in diethylene glycol dimethyl ether (diglyme)^{1,2}, tetrahydrofuran–borane³, bis(1,2-dimethylpropyl)borane (disiamylborane)⁴, dimethyl sulfide–borane⁵ or 9-borabicyclo[3.3.1]nonane⁵. However, hydroboration of styrene containing a substituent with tertiary amino group has not been studied so far.

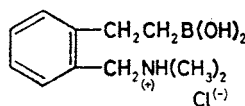
We hydroborated N,N-dimethyl(2-vinylbenzyl)amine (*Ia*) with triethylamine–borane. The reaction afforded a 2 : 1 mixture of 1,1-dimethyl-5,6-benzo-1-aza-2-boracycloheptane (*IIa*) and 1,1,3-trimethyl-4,5-benzo-1-aza-2-boracyclohexane (*IIb*),



- Ia*, R = CH=CH₂
Ib, R = CH₂CH₂B(OC₂H₅)₂
Ic, R = CH₂CH₂OH
Id, R = CH(OH)CH₃
Ie, R = C₂H₅
If, R = CH₂CH₂-B



- IIa*, Z = (CH₂)₂
IIb, Z = CHCH₃



III

inseparable by distillation. After the hydrolysis of the mixture with hydrochloric acid we were able to isolate only 2-(2-dimethylaminomethylphenyl)ethylboronic acid

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hydrochloride (*III*) which on ethanolysis gave diethyl 2-(2-dimethylaminomethylphenyl)ethylboronate (*Ib*).

In order to study the ratio of the products with the boron atom in the α - and β -position relative to the benzene ring and to investigate how this ratio can be affected, we hydroborated the compound *Ia* with four hydroborating reagents: triethylamine-borane, diborane generated *in situ* from sodium borohydride and boron trifluoride diethyl etherate, 9-borabicyclo[3.3.1]nonane, and tetrahydrofuran-borane. The hydroboration products were hydrolyzed with hydrochloric acid and oxidized with hydrogen peroxide in an alkaline medium. The obtained mixtures were analyzed by gas-liquid chromatography and the results are summarized in Table I.

Reaction of all the reagents, except 9-borabicyclo[3.3.1]nonane, afforded 2-(2-dimethylaminomethylphenyl)ethanol (*Ic*), 1-(2-dimethylaminomethylphenyl)ethanol (*Id*), and 2-(dimethylaminomethylphenyl)ethylbenzene (*Ie*). With 9-borabicyclo[3.3.1]nonane we found, as expected⁵, only the alcohol *Ic*; however, the preparation of *Ic* by reaction of *Ia* with this reagent is not suitable because the alcohol *Ic* cannot be separated by distillation from 1,5-cyclooctanediol formed from the reagent.

The reaction with diborane *in situ* was performed at 20°C. The hydroboration product was worked up as described above either directly or after heating to 150°C for 3 hours: both procedures gave identical product mixtures.

The reaction of compound *Ia* with tetrahydrofuran-borane was carried out using 1 : 1 or 1 : 2 molar ratio. In the first case a part of the substrate was recovered. We also studied the dependence of the product mixture composition on the period of time (15 min to 4 h) between the addition of *Ia* to the reagent and the acid hydrolysis. The hydroboration reaction was complete already after 15 min because in all cases (1 : 1 ratio of the reactants) we found practically the same ratio of *Ic* to *Ia*. On the other hand, the ratio *Id* : *Ie* irregularly varied. Since the amount of *Ie* increased substantially when the alkaline reaction mixture was heated for 1 h before addition of hydrogen peroxide whereas prolonged treatment with hydrochloric acid had no effect, it is obvious that *Ie* arises by alkaline hydrolysis, concurrently with the oxidation, mainly from hydroboration products with the boron atom α to the benzene ring.

The relation between substitution and the selectivity of hydroboration of styrenes has been already studied¹⁻⁵. However, the effect of the dimethylaminomethyl group on the hydroboration selectivity cannot be compared with the published results since in all hitherto described cases one molecule of the hydroboration reagent reacted with three molecules of the substituted styrene. Thus, such reactions involved three consecutive hydroboration steps with three hydroboration reagents: Hydroboration of the starting styrene with the original reagent to monoalkylborane, hydroboration of the starting styrene with the monoalkylborane to dialkylborane and hydroboration of the starting styrene with the dialkylborane to trialkylborane. Since

disubstituted boranes such as 9-borabicyclo[3.3.1]nonane⁵ or disiamylborane⁴ add to double bonds highly selectively in an anti-Markovnikov fashion whereas the hydroboration of styrene with diborane *in situ*¹ or with tetrahydrofuran–borane³ leads predominantly to the primary alcohol (80%), the individual steps probably differ considerably in selectivity.

The hydroboration of *Ia* is complicated by the presence of the dimethylamino group. Reaction with triethylamine–borane, diborane *in situ*, and tetrahydrofuran–borane in which the actual hydroboration reagent is the BH₃ molecule, can give rise primarily to N,N-dimethyl-(2-vinylbenzyl)amine–borane (*IVa*) which is then hydroborated. On heating, the separately prepared compound *IVa* was transformed into hydroboration products whereas at room temperature it was stable. If the double bond in *Ia* is hydroborated first, the C–BH₂ grouping can be stabilized – and deactivated – by formation of intramolecular (under formation of cyclic amine–borane *Iia* or *Iib*) or intermolecular (dimer formation) B←N bond. On the other hand, the C–BH₂ group can attack the double bond of another molecule before the mentioned stabilization takes place, or after addition of another molecule of BH₃ to the nitrogen atom.

Triethylamine–borane reacted with compound *Ia* only at a temperature enabling dissociation of amine–boranes. Whereas we cannot decide whether, under these

TABLE I

Relative molar population of *Ic*–*Ie* after hydroboration and oxidation

Substrate	Reagent ^a	<i>Ic</i> ^b	<i>Id</i>	<i>Ie</i> ^c
<i>Ia</i>	Et ₃ N.BH ₃	67.5	32.2	0.3
<i>Ia</i>	borane <i>in situ</i>	67.3	30.0	2.7
<i>Ia</i>	9-BBN	100	0	0
<i>Ia</i>	THF.BH ₃ ^{d,e,f}	65.3	25.0	9.7
<i>Ia</i>	THF.BH ₃ ^{e,g}	63.7	26.8	9.5
<i>Ia</i>	THF.BH ₃ ^{e,h}	64.5	34.6	0.9
<i>Ia</i>	THF.BH ₃ ^{e,i}	61.7	11.5	26.8
<i>IVa</i>	THF.BH ₃	63.1	27.6	9.2
<i>IVb</i>	THF.BH ₃	65.0	33.3	1.7

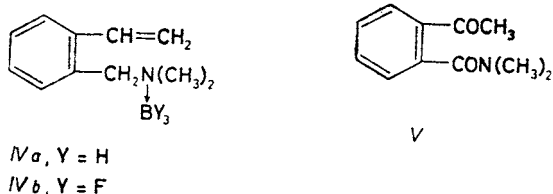
^a Et₃N.BH₃ triethylamine–borane, 9-BBN 9-borabicyclo[3.3.1]nonane, THF.BH₃ tetrahydrofuran–borane; ^b standard prepared according to ref.⁶; ^c standard prepared according to ref.⁷; ^d molar ratio of substrate to hydroboration reagent 1 : 1; ^e mean values determined for the successively withdrawn samples; ^f recovered 23.1% of *Ia*; ^g molar ratio of substrate to hydroboration reagent 1 : 2; ^h remaining hydroboration product; hydrogen peroxide added immediately after addition of the base; ⁱ remaining hydroboration product; the alkaline mixture boiled for 1 h prior to addition of hydrogen peroxide.

conditions, a dative bond between the nitrogen and boron atom temporarily arises or not, we consider this reaction proven for the hydroboration with tetrahydrofuran–borane. The fact that in the 1 : 1 hydroboration experiment the reaction mixture contains the starting compound *Ia* can be explained only by blocking a part of the reagent whose quantity is consequently not sufficient for complete hydroboration. We assume an analogous pathway also for the reaction of *Ia* with diborane *in situ* at 20°C. The dimethylamino group does not affect the composition of the final mixture in the reaction with 9-borabicyclo[3.3.1]nonane. Thus, if at all, the boron atom of this reagent is attacked by the free electron pair of the nitrogen atom, the corresponding complex is not stable under the reaction conditions.

Some comparison with previous results^{1–3} is, however, possible for hydroboration of N,N-dimethyl-(2-vinylbenzyl)amine–borane (*IVa*) and N,N-dimethyl-(2-vinylbenzyl)amine–trifluoroborane (*IVb*) which afford with tetrahydrofuran–borane the primary alcohol *Ic* in the respective yields of 63% and 65% (Table I). Thus, the $\text{CH}_2\text{N}(\text{CH}_3)_2\text{—BY}_3$ (Y = H or F) groups resemble most the trifluoromethyl group².

Characterization of the obtained compounds and analyses of the reaction mixtures were done by IR and NMR spectra; the relevant data are given in the Experimental. Formation of a bond between the boron atom and the nitrogen atom of the dimethylamino group in all hydroborations of *Ia* is shown by marked downfield shifts of NMR signals of the $(\text{CH}_3)_2\text{NCH}_2$ protons (0.2–0.4 ppm for methyl and 0.6 to 0.8 ppm for CH_2 signals). According to the shape of the spectral bands we assume (more or less intuitively) the formation of cyclic species of the type *II* rather than of polymeric chains.

As shown by ¹¹B NMR spectra, in the reaction mixture after heating the amine–borane *IVa* all the boron atoms are bonded in compounds *IIa, b*; the same is true for the hydroboration product from *Ia* and triethylamine–borane. However, in other cases the ¹¹B NMR spectrum of the products contains a greater number of signals which we were not able to assign and which do not exclude the possibility of further alkylation of the boron atoms. Because of experimental difficulties, it was not possible to separate and identify the individual components of these mixtures.



The products of hydroboration of *Ia*, hydrolysis and oxidation were identified by gas–liquid chromatographic comparison with independently prepared standards.

The hitherto unknown alcohol *Id* was prepared by lithium aluminium hydride reduction of *N,N*-dimethyl-2-acetylbenzamide (*V*) which in turn was obtained by reaction of 2-acetylbenzoyl chloride with dimethylamine.

EXPERIMENTAL

The temperature data are uncorrected. Gas-liquid chromatography was performed on a Chrom 5 chromatograph equipped with a CI 100 integrator (Laboratorní přístroje, Prague); detection with flame-ionization detector. Compounds were identified using 2 500 × 3 mm glass columns packed with 10% silicone E 301 on Chromaton A-AW-DMCS (particle size 0.16–0.20 mm) or 3% silicone OV-225 on Chromaton N-AW-DMCS (0.125–0.16 mm). Quantitative analyses were run on the latter column. Temperature programme 130–220°C, 5°C/min, carrier gas nitrogen, flow rate 30–40 ml/min. The relative detector responses (weight) to the compounds were not determined and were taken as identical. Infrared spectra were measured on a Perkin-Elmer 325 spectrophotometer, NMR spectra on a Varian XL-100-15 (100.1 MHz for ¹H and 32.1 MHz for ¹¹B) or a Bruker AM 400 (400.133 MHz for ¹H and 128.380 MHz for ¹¹B) instrument. The proton spectra were taken with tetramethylsilane (in deuteriochloroform) or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (in deuterium oxide) as internal standards. For the ¹¹B NMR spectral measurements trimethyl borate was used as external standard. Chemical shifts downfield from those of the standard are taken as positive. Chemical shifts in the ¹¹B NMR spectra were related to boron trifluoride diethyl etherate as standard by adding 18.1 ppm.

N,N-Dimethyl-(2-vinylbenzyl)amine (*Ia*)

A solution of 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium iodide⁸ (33.0 g; 114 mmol) in water (100 ml) was added to a suspension of silver oxide (prepared from 25.2 g; 148 mmol of silver nitrate in water). After stirring for 1 h, the mixture was filtered. The filtrate which contained no iodide ions was concentrated *in vacuo* to about 60 ml and the residue was distilled *in vacuo*. The distillate (b.p. 25–125°C/2.7 kPa, 56.5 g) was extracted with diethyl ether, the extract was dried over magnesium sulfate and the solvent was evaporated. Yield 9.6 g (52%) of *Ia*, b.p. 107–109°C/2.7 kPa (reported⁹ b.p. 102°C/2.3 kPa). ¹H NMR spectrum (C²HCl₃): 2.01 to 2.20 m, 6 H (2 CH₃); 3.38 s, 2 H (CH₂—N); 5.21 d, 1 H ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$, *J* = 11 Hz); 5.58 d, 1 H ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$, *J* = 18 Hz); 6.95–7.69 m, 5 H (C₆H₄—CH=).

Reaction of *Ia* with Triethylamine-Borane

A mixture of *Ia* (8.0 g; 50 mmol) and triethylamine-borane (ref.¹⁰, 5.7 g; 50 mmol) was slowly heated under nitrogen in a flask equipped with a reflux condenser. The reaction started at 130°C (reflux) and the bath temperature was increased to 150°C. After cooling, triethylamine (3.8 g; 76%) was distilled from the reaction mixture. Distillation of the residue gave 3.9 g (45%) of an oil, b.p. 83–85°C/1.3 Pa, consisting of *Ila* (65%) and *Ilb* (35%). For C₁₁H₁₈BN (175.1) calculated: 75.46% C, 10.36% H, 6.18% B, 8.00% N; found: 75.40% C, 10.56% H, 6.14% B, 7.87% N. ¹H NMR spectrum (C²HCl₃): 0.46–0.84 m (CH₂—B in *Ila*); 1.10 d (C—CH₃ in *Ilb*, *J* = 6 Hz); 2.5 s (N(CH₃)₂ in *Ila*); 2.56 s and 2.63 s (N(CH₃)₂ in *Ilb*); 2.8–3.05 m (Ar—CH₂—C in *Ila* and Ar—CH—B in *Ilb*); 3.6–4.15 m (CH₂—N in *Ila,b*); 6.9–7.55 m (H_{arom}). ¹¹B NMR spectrum (C²HCl₃): -5.6 t (N→BH₂ in *Ilb*, *J* = 97 Hz); -2.6 t (N→BH₂ in *Ila*, *J* = 97 Hz).

2-(2-Dimethylaminomethylphenyl)ethylboronic Acid Hydrochloride (*III*)

Hydrochloric acid (15%; 9 ml) was added dropwise under stirring to a solution of the mixture of amine-boranes *Ila* and *Iib* obtained in the preceding experiment (2.6 g; 15 mmol) in acetone (15 ml). After reflux for 15 min and evaporation *in vacuo*, the residue was repeatedly crystallized to afford 0.8 g (22%) of *III*, m.p. 119–121°C (acetone). For $C_{11}H_{19}BClNO_2$ (243.5) calculated: 54.25% C, 7.86% H, 4.44% B, 14.56% Cl, 5.75% N; found: 54.25% C, 7.84% H, 4.52% B, 14.69% Cl, 5.85% N. 1H NMR spectrum (2H_2O): 1.01 t, 2 H (CH_2-B , $J = 7$ Hz); 2.58–2.89 m, 8 H (CH_2-C-B and 2 CH_3); 4.27 s, 2 H (CH_2-N); 7.10–7.41 m, 4 H (H_{arom}).

Diethyl 2-(2-Dimethylaminomethylphenyl)ethylboronate (*Ib*)

A solution of compounds *Ila* and *Iib* (1.8 g; 10 mmol) in ethanol (15.4 ml) was refluxed for 23 h. After evaporation of ethanol, the product was fractionated and two fractions were collected: *a*) b.p. 75–86°C/1.3 Pa (0.7 g), and *b*) b.p. 87–88°C/1.3 Pa (0.4 g). According to TLC (Alufol, in benzene), fraction *a*) consisted of the starting amine-boranes and alcoholysis products, fraction *b*) was the alcoholysis product which on distillation (b.p. 84–88°C/1.3 Pa) gave 0.3 g (11%) of *Ib*. For $C_{15}H_{26}BNO_2$ (263.2) calculated: 68.45% C, 9.96% H, 4.11% B, 5.32% N; found: 68.50% C, 9.77% H, 4.46% B, 5.61% N. 1H NMR spectrum (C^2HCl_3): 0.80–1.40 m, 2 H (CH_2-B); 1.18 t, 6 H (2 CH_3 , $J = 7$ Hz); 2.56–2.92 m, 2 H (CH_2-C-B); 2.25 s, 6 H ($N(CH_3)_2$); 3.41 s, 2 H (CH_2-N); 3.82 q, 4 H (2 $O-CH_2$, $J = 7$ Hz); 7.02–7.40 m, 4 H (H_{arom}).

Hydrolysis and Oxidation of Reaction Product from *Ia* and Triethylamine-Borane

Compound *Ia* (3.2 g; 20 mmol) and triethylamine-borane¹⁰ (2.3 g; 20 mmol) were reacted and triethylamine was distilled off. The product was dissolved in acetone (20 ml) and 15% hydrochloric acid (12 ml) was added with stirring so as the hydrogen evolution was not too vigorous. After reflux for 15 min with stirring, the solvent and the excess acid were evaporated *in vacuo*, the residue was suspended in tetrahydrofuran (20 ml) and 3M-NaOH (30 ml) was added to the stirred mixture. Hydrogen peroxide (30%; 3.0 ml) was added dropwise with stirring, the mixture was stirred at room temperature for 1 h and saturated with potassium carbonate. The organic layer was separated, the aqueous one extracted with diethyl ether (3 × 10 ml) and the combined organic layers were dried over potassium carbonate. After evaporation of the solvents, the residue was distilled affording the following fractions: *a*) b.p. 132–145°C/3.3 kPa (0.6 g), *b*) b.p. 145 to 152°C/3.3 kPa (0.75 g), and *c*) b.p. 152°C/3.3 kPa (1.25 g). Gas chromatographic analysis showed that fraction *a*) contained *Ic* (58%), *Id* (41%), and *Ie* (1%), fraction *b*) *Ic* (63%) and *Id* (37%), and fraction *c*) *Ic* (75%) and *Id* (25%). These data correspond to the mixture of composition given in Table I (total amount 2.6 g (73%)).

Reaction of *Ia* with Diborane *in situ*

Compound *Ia* (1.6 g; 10 mmol) was added to a suspension of sodium borohydride (0.4 g; 10 mmol) in diglyme (15 ml). A solution of boron trifluoride diethyl etherate (1.8 ml; 14 mmol) in diglyme (3.5 ml) was added dropwise during 15 min under nitrogen at bath temperature 20°C. After stirring for 1 h, the first sample (2.0 ml) was taken through a rubber septum by means of a syringe. The bath temperature was increased to 150°C during 15 min. Immediately after achieving this temperature, a second sample was withdrawn and (at the same temperature) further three samples were taken in 1 h intervals. Each sample was decomposed with 15% hydrochloric acid (0.8 ml), and then tetrahydrofuran (2.0 ml), 40% NaOH (1.0 ml), and 30% H_2O_2 (0.7 ml) were successively

added. After reflux with stirring for 1 h, each sample was saturated with potassium carbonate, the organic layer was separated and the aqueous one was extracted with diethyl ether (2×3 ml). The extracts were combined with the original organic layers and analyzed by gas-liquid chromatography; all had the same composition (Table I).

Reaction of *Ia* with 9-Borabicyclo[3.3.1]nonane

A solution of *Ia* (2.02 g; 12.5 mmol) in tetrahydrofuran (6.5 ml) was added to a suspension of 9-borabicyclo[3.3.1]nonane¹¹ (1.53 g; 12.5 mmol) in tetrahydrofuran (12.5 ml) and the mixture was refluxed for 3 h with stirring in a nitrogen atmosphere. The mixture was cooled and 3M-NaOH (4.2 ml) was added, followed (with stirring) by 30% H₂O₂ (4.2 ml; vigorous reaction). After reflux with stirring for 1 h, the mixture was cooled, the organic layer was separated, the aqueous one was extracted with tetrahydrofuran (3×5 ml), the extract was combined with the original organic layer and dried over potassium carbonate. The tetrahydrofuran solution contained 1.39 g (62%) of *Ic* and 1.32 g (73%) of 1,5-cyclooctanediol (according to gas-liquid chromatography).

In a separate experiment, tetrahydrofuran was evaporated *in vacuo* at 25°C from the hydroboration mixture. Proton NMR spectroscopy showed that the product contained 2-dimethylaminomethyl-(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)benzene (*If*). ¹H NMR spectrum (C²HCl₃): 0.6–0.8 m, 2 H (>CH—B—CH<); 1.05–1.2 m, 2 H (CH₂—B); 1.2–2.5 m, 12 H (2(CH₂)₃); 2.53 s, 6 H ((CH₃)₂N); 2.9–3.1 m, 2 H (Ar—CH₂—C); 3.75 s, 2 H (CH₂—N); 7.0–7.4 m, 4 H (H_{arom}). ¹¹B NMR (C²HCl₃): 22.1 s ($\text{C} \begin{array}{c} \curvearrowright \\ \text{B—C} \end{array}$) and minor broad signals –7.5, 0, 6, and 50.

Reaction of *Ia* with Tetrahydrofuran–Borane

A) A solution of *Ia* (0.5 g; 3.1 mmol) in tetrahydrofuran (12 ml) was added dropwise during 5 min at room temperature to a stirred 1.47M-tetrahydrofuran–borane solution¹² (2.1 ml; 3.1 mmol) in a nitrogen atmosphere. After stirring for 1 h, most of the tetrahydrofuran was evaporated *in vacuo* at 25°C. ¹H NMR spectrum in deuteriochloroform showed a mixture of tetrahydrofuran, *Ia* and compounds containing (CH₃)₂N→B bonds. Signals of CH₂—B and CH—B were located between 0.4 and 1.1 ppm. ¹¹B NMR spectrum (C²HCl₃) proved two types of —BH₂ groupings (–8.7 t, *J* = 86 Hz and –5.6 t, *J* = 92 Hz). In addition, broad singlets at –13.7 and –12.3 and a doublet at 21.9 (*J* = 129 Hz) were present. A more detailed assignment of the signals was not possible.

B) A solution of *Ia* (1.0 g; 6.2 mmol) in tetrahydrofuran (12 ml) was added dropwise during 5 min at room temperature under nitrogen to a stirred 1.47M-tetrahydrofuran–borane solution¹² (4.2 ml; 6.2 mmol). The mixture was further stirred under the same conditions and 2.0 ml samples were withdrawn 15 min, 1 h, 2 h, and 4 h after the beginning. Each sample was decomposed with 15% hydrochloric acid (1.7 ml), diluted with tetrahydrofuran (3.5 ml), and made alkaline with 40% NaOH (3.5 ml). After addition of 30% H₂O₂ (1.7 ml), the mixture was refluxed with stirring for 1 h, cooled and saturated with potassium carbonate. The organic layer was separated, the aqueous one was extracted with tetrahydrofuran (2×2.5 ml), the extract was combined with the original organic layer and the resulting product was dried over potassium carbonate and analyzed by gas-liquid chromatography (Table I).

C) The experiment was carried out as described under B) but with only half amount of *Ia* (0.5 g; 3.1 mmol). After withdrawal of the last sample, the remaining solution of the hydroboration product was decomposed with 15% HCl (4 ml) and set aside for 3 days. After dilution with tetrahydrofuran (7 ml), one half of the solution was worked up in the same manner as the

withdrawn samples. The other half was mixed with 40% NaOH (3.5 ml), the mixture was refluxed under stirring for 1 h and then processed as described in the previous experiments. The analytical results are given in Table I.

N,N-Dimethyl-(2-vinylbenzyl)amine-borane (*IVa*) and Its
Thermal Transformation

Water (6.2 ml) was added dropwise under nitrogen to a stirred suspension of N,N-dimethyl-(2-vinylbenzyl)amine hydrochloride¹³ (4.94 g; 25 mmol) and sodium borohydride (1.18 g; 31.2 mmol) in diethyl ether (25 ml) so as the hydrogen evolved moderately (in the course of several minutes). After further 10 min of stirring, the mixture was filtered, the aqueous layer separated, the organic layer dried over potassium carbonate and the solvent evaporated *in vacuo* at room temperature. The residue (3.28 g; 77%) consisted of *IVa* (73%) and *Ia* (27%). For 73% of C₁₁H₁₈BN (175.1) and 27% of C₁₁H₁₅N (161.2) calculated: 77.21% C, 10.09% H, 4.51% B, 8.19% N; found: 77.15% C, 9.76% H, 4.59% B, 8.01% N. ¹H NMR spectrum (C²HCl₃): 2.22 s (N(CH₃)₂ in *Ia*); 2.48 s (N(CH₃)₂ in *IVa*); 3.42 s (N—CH₂ in *Ia*); 4.13 s (N—CH₂ in *IVa*); 5.28–5.31 m ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$ in *Ia*); 5.39–5.42 m ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$ in *IVa*); 5.63–5.70 m ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ = $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ in *Ia*); 5.67–5.73 m ($\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$ in *IVa*); 7.0–7.6 m (C₆H₄—CH=). ¹¹B NMR spectrum (C²HCl₃): –13.7 q (*J* = 94 Hz). IR spectrum (CCl₄) ν , cm⁻¹: 1 168 s δ (BH), 2 370 s ν (BH).

Distillation of the product (2.69 g; 82%) afforded 0.74 g (22%) of *Ia*, b.p. 53°C/40 Pa (identified by elemental analysis and by ¹H NMR and IR spectra), and 0.85 g (24%) of a liquid, identified as a 74 : 26 mixture of *Ila* and *Ilb*. For C₁₁H₁₈BN (175.1) calculated: 75.46% C, 10.36% H, 6.18% B, 8.00% N; found: 75.77% C, 10.37% H, 5.71% B, 8.30% N. ¹¹B NMR spectrum (C²HCl₃): –8.6 t (BH₂ in *Ilb*, *J* = 93.8 Hz); –5.6 t (BH₂ in *Ila*, *J* = 89 Hz). ¹H NMR spectrum identical with that described in the paragraph Reaction of *Ia* with Triethylamine-Borane.

Hydroboration of *IVa* with Tetrahydrofuran-Borane

N,N-Dimethyl-(2-vinylbenzyl)amine hydrochloride¹³ (6.72 g; 34 mmol) was hydroborated with sodium borohydride (1.61 g; 42.5 mmol) as described in the preceding experiment to give a mixture (5.44 g; 92%) of *IVa* (86%) and *Ia* (12%). For 88% of C₁₁H₁₈BN (175.1) and 12% of C₁₁H₁₅N (161.2) calculated: 76.24% C, 10.24% H, 5.44% B, 8.08% N; found: 76.12% C, 9.97% H, 5.73% B, 8.15% N. A solution of this mixture (5.25 g; 96.5% of the total amount) in tetrahydrofuran (120 ml) was added dropwise under nitrogen at room temperature to 1.47M-tetrahydrofuran-borane¹² (23.1 ml, 34 mmol) in the course of 10 min. After stirring for 1 h, 15% HCl (8 ml) was added (evolution of hydrogen), the mixture was refluxed with stirring for 15 min, cooled, made alkaline with 40% NaOH (8 ml) and 30% H₂O₂ was added (exothermic reaction). After reflux with stirring for 1 h, potassium carbonate was added to saturation. The organic layer was separated, the aqueous one was extracted with tetrahydrofuran (3 × 10 ml) and the extract was combined with the original organic layer. According to gas-liquid chromatography, the solution contained 0.048 g (9%) of *Ie*, 1.58 g (27%) of *Id* and 3.61 g (61%) of *Ic*.

Hydroboration of N,N-Dimethyl-(2-vinylbenzyl)amine-Trifluoroborane (*IVb*) with Tetrahydrofuran-Borane

A solution of boron trifluoride diethyl etherate (2.0 ml; 15.6 mmol) in tetrahydrofuran (20 ml) was added dropwise under nitrogen at room temperature to a stirred solution of *Ia* (2.42 g;

15 mmol) in tetrahydrofuran (40 ml) in the course of 5 min. After further 15 min of stirring, a sample (6 ml, 9%) was withdrawn from which volatile components were evaporated *in vacuo* at room temperature. According to NMR spectrum, the residue contained *IVb*. ^1H NMR spectrum (C^2HCl_3): 2.45 s, 6 H ($\text{N}(\text{CH}_3)_2$); 2 H ($\text{CH}_2\text{-N}$); 5.43 dd, 1 H ($\text{H} \text{---} \text{C}=\text{C} \begin{matrix} \text{H} \\ \text{H} \end{matrix}$, $^3J = 9$ Hz, $^2J = 2$ Hz); 5.72 dd, 1 H ($\text{H} \text{---} \text{C}=\text{C} \begin{matrix} \text{H} \\ \text{H} \end{matrix}$, $^3J = 17$ Hz, $^2J = 2$ Hz); 7.02 dd, 1 H (Ar-CH=); 7.25–7.65 m, 4 H (H_{arom}). ^{11}B NMR spectrum (C^2HCl_3): -5.2 q ($J(\text{B}, \text{F}) = 15.2$ Hz).

The remaining solution was added dropwise in a nitrogen atmosphere at room temperature to a stirred 1.47M-tetrahydrofuran-borane solution¹² (10.2 ml; 15 mmol) during 10 min. The mixture was stirred for 1 h at room temperature, cooled in an acetone-dry ice bath, and 3M-NaOH (25 ml) was added with stirring (evolution of hydrogen and partial solidification). After addition of 30% H_2O_2 (10 ml), the mixture was refluxed with stirring for 1 h, cooled and saturated with potassium carbonate. The organic layer was separated, the aqueous one was extracted with tetrahydrofuran (3 \times 5 ml), the extract was combined with the original organic layer and dried over potassium carbonate. According to gas-liquid chromatography, the solution contained *Ic* (1.03 g; 46%), *Id* (0.528 g; 24%), and *Ie* (0.024 g; 1%).

N,N-Dimethyl-2-acetylbenzamide (*V*)

A solution of dimethylamine in toluene was added with stirring to a solution of 2-acetylbenzoyl chloride¹⁴ (17.0 g; 93 mmol) in diethyl ether (200 ml) until the mixture was alkaline. The suspension was stirred for 1 h and filtered, the filtrate was taken down *in vacuo* and the residue was crystallized from cyclohexane to give 9.75 g (55%) of *V*, m.p. 78–80°C. For $\text{C}_{11}\text{H}_{13}\text{NO}_2$ (191.2) calculated: 69.09% C, 6.85% H, 7.32% N; found: 68.98% C, 7.15% H, 7.23% N. ^1H NMR spectrum (C^2HCl_3): 2.58 s, 3 H, 2.75 s, 3 H, and 3.13 s, 3 H (3 CH_3); 7.19–7.92 m, 4 H (H_{arom}). IR spectrum (CHCl_3) ν , cm^{-1} : 1 630 $\nu(\text{C=O})$ in N-CO ; 1 685 $\nu(\text{C=O})$ in $\text{CH}_3\text{-CO}$.

1-(2-Dimethylaminomethylphenyl)ethanol (*Id*)

A solution of amide *V* (3.0 g; 16 mmol) in diethyl ether (190 ml) was added dropwise during 35 min to a stirred suspension of 95% lithium aluminium hydride (1.0 g; 25 mmol) in diethyl ether (120 ml). After reflux for 6 h with stirring, the mixture was decomposed with 4% NaOH (3.9 ml) and filtered. The filtrate was dried over potassium carbonate and the solvent distilled off to give 2.05 g (73%) of *Id*, b.p. 118–122°C/1.3 kPa. For $\text{C}_{11}\text{H}_{17}\text{NO}$ (179.2) calculated: 73.73% C, 9.56% H, 7.82% N; found: 73.69% C, 9.59% H, 8.02% N. ^1H NMR spectrum (C^2HCl_3): 1.58 d, 3 H (C-CH_3 , $J = 6.5$ Hz); 2.24 d, 6 H ($\text{N}(\text{CH}_3)_2$); 3.18 d, 1 H and 3.93 d, 1 H ($\text{CH}_2\text{-N}$, $J = 12$ Hz); 4.97 q, 1 H (CH-O , $J = 6.5$ Hz); 7.06–7.54 m, 5 H (H_{arom} and OH).

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