HYDROBORATION OF 1,4-DIALLYLPIPERAZINE*

Stanislav KAFKA and Miloslav FERLES

Department of Organic Chemistry
Prague Institute of Chemical Technology, 166 28 Prague 6

Received June 14th, 1984

Hydroboration of 1,4-diallylpiperazine (*I*) with triethylamine-borane afforded 5,8-diaza-1,9-diboradispiro[4,2,4,2]tetradecane (*II*). 1,4-Diallylpiperazine dihydrochloride reacted with sodium borohydride to give 1,4-diallylpiperazine-diborane (*V*). Ethanolysis of *II* furnished 1,4-bis(3-diethoxyborylpropyl)piperazine (*IV*). The products of hydroboration of *I* were subjected to hydrolysis with hydrochloric acid and subsequent oxidation with alkaline hydrogen peroxide and the obtained mixtures were analyzed by gas–liquid chromatography and mass spectrometry.

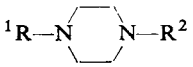
In our previous communications[1-3] we described hydroboration of N-alkenyl derivatives of cyclic amines with triethylamine-borane which gave spirocyclic amine-boranes in good yields. Within the framework of these investigations, it was of interest to study the hydroboration of 1,4-diallylpiperazine (*I*). Reaction of this compound with triethylamine-borane, performed as described previously for N-alkenylazacycloalkanes[1-3], afforded 5,8-diaza-1,9-diboradispiro[4,2,4,2]tetradecane (*II*). The structure of *II* was confirmed by its ^{1}H NMR spectrum in which the signals of methylenes bonded to the nitrogen atoms appeared downfield as compared with those in the spectra of 1,4-disubstituted piperazines[4]. This corresponds to a lower electron density at the nitrogen atoms caused by formation of the $\equiv\overset{\delta+}{N}\!-\!\overset{\delta-}{B}H_2\!-\!C$ bonds. The existence of coordinative bonds B—N is also indicated by the high stability of compound *II* which remained unchanged upon storage and exposure to air for one year at room temperature.

Infrared spectrum of compound *II* exhibits absorption bands due to B—H bond deformation and stretching vibrations at 1 190 cm^{-1} and 2 205–2 390 cm^{-1}, respectively, the assignment being made by comparison with the corresponding vibrations in 1,1-dimethyl-1-aza-2-boracyclohexane[5]. No C=C stretching vibration was found; the absence of bands in the region 1 970–2 150 cm^{-1} indicates the absence of B—H—B bridges[6].

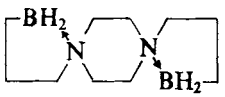
We tried to decide whether the boron atoms in *II* are *cis* or *trans* to the central ring by means of dipole moment measurement. The values of dipole moments de-

* Part XVII in the series Hydroboration of Unsaturated Amines; Part XVI: This Journal *50*, 1194 (1985).

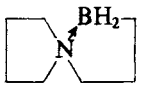
termined for various amine-boranes vary in the range 3·60–5·86 D (refs[7–10]). For 5-aza-1-boraspiro[4,4]nonane (*III*, ref.[1]) which we chose as a model compound, the dipole moment was determined to be $\mu_5 = 4{\cdot}32$ D and $\mu_{15} = 4{\cdot}31$ D, depending on the atomic polarization contribution estimated to be 5% and 15% of the molar refraction, respectively. For the compound *II* the respective dipole moments are $\mu_5 = 0{\cdot}98$ D and $\mu_{15} = 0{\cdot}82$ D. Since these values are lower than those for the monofunctional amine-boranes, we assume that the compound *II* has *trans*-configuration.



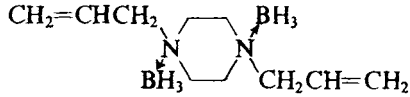
I, $R^1 = R^2 = CH_2CH{=}CH_2$
IV, $R^1 = R^2 = (CH_2)_3B(OCH_2CH_3)_2$
VI, $R^1 = R^2 = (CH_2)_3OH$
VII, $R^1 = CH_2CH_2CH_3$, $R^2 = (CH_2)_3OH$
VIII, $R^1 = H$, $R^2 = (CH_2)_3OH$
IX, $R^1 = H$, $R^2 = CH_2CH(OH)CH_3$
X, $R^1 = CH_2CH_2CH_3$, $R^2 = CH_2CH(OH)CH_3$
XI, $R^1 = CH_2CH(OH)CH_3$, $R^2 = (CH_2)_3OH$
XII, $R^1 = CH_2CH{=}CH_2$, $R^2 = CH_2CH(OH)CH_3$
XIII, $R^1 = CH_2CH{=}CH_2$, $R^2 = (CH_2)_3OH$
XIV, $R^1 = R^2 = CH_2CH(OH)CH_3$



II



III



V

The crude reaction product from reaction of compound *I* with triethylamine-borane on treatment with ethanol afforded 1,4-bis(3-diethoxyborylpropyl)piperazine (*IV*). The low yield (13%) of compound *IV* indicates its formation by ethanolysis of *II* present in the reaction mixture. According to the NMR spectra, compound *IV* contains no dative B—N bonds. The proton signals of the nitrogen-bonded methylene groups occur at the same positions as the corresponding signals in the spectra of 1,4-disubstituted piperazines[4]. The ^{11}B NMR signal (+29·3 ppm) is located near the positions at which the signals of esters of non-nitrogen boronic acids occur[11,12].

In order to improve the yields, we tried to prepare *II via* 1,4-diallylpiperazine-diborane (*V*) by reaction of 1,4-diallylpiperazine dihydrochloride with sodium borohydride and subsequent heating. Although this method works in the preparation of 1,1-dimethyl-1-aza-2-boracycloalkanes[9], it failed in this case, affording the amine-borane *V* in only 17% yield. The structure of *V* has been proved by its NMR and IR spectra. Thanks to the positive charge at the nitrogen atoms, all the ^1H NMR

signals are shifted downfield relative to those of compound *I* (ref.[4]). The signal in the ^{11}B NMR spectrum (−13·4 ppm) corresponds to a BH_3 group bonded to a nitrogen atom[11,13]. The IR spectrum displays bands due to B—H deformation vibration (1 190 cm^{-1}), B—H stretching vibration (2 290−2 420 cm^{-1}) and B—N stretching vibration (1 000 cm^{-1} and 1 165 cm^{-1}). The last-mentioned absorption bands were identified by comparison with the published[13] B—N vibrations for a series of compounds containing a BH_3 group bonded coordinatively to nitrogen.

When the compound *V* was heated in a nitrogen atmosphere, it exploded at 97°C. Heating a solution or suspension of this compound in xylene or dibutyl ether to 120°C under nitrogen afforded mixtures in which no compound *II* could be detected.

The reaction product of *I* with triethylamine-borane on boiling with hydrochloric acid in acetone and subsequent oxidation with hydrogen peroxide in alkaline medium gave a mixture containing 1,4-bis(3-hydroxypropyl)piperazine (*VI*) as the principal product. After isolation of compound *VI* and partial separation by column chromatography, we identified the following compounds by ^1H NMR spectroscopy: 3-(4-propyl-1-piperazinyl)-1-propanol (*VII*), 3-(1-piperazinyl)-1-propanol (*VIII*), 1-(1-piperazinyl)-2-propanol (*IX*) and 1-(4-propyl-1-piperazinyl)-2-propanol (*X*). This finding indicated that the mixtures after hydroboration, hydrolysis and oxidation of compound *I* might contain, in addition to compounds *VI*−*X*, also other piperazine derivatives with the following substituents in positions 1 and 4: 3-hydroxypropyl group, 2-hydroxypropyl group, propyl group or hydrogen.

To check this possibility, we performed the hydroboration of *I* using three procedures: with triethylamine-borane, with sodium borohydride and boron trifluoride etherate in tetrahydrofuran, and with the same reagents in diethylene glycol dimethyl ether (diglyme). The hydroboration products were subjected to hydrolysis with hydrochloric acid and subsequent oxidation with hydrogen peroxide and the mixtures were analyzed by gas–liquid chromatography and mass spectrometry using independently prepared standards[4]. The product obtained by hydroboration of *I* with triethylamine-borane was found to contain compounds *VI*−*IX*, 1-(4-propyl--1-piperazinyl)-2-propanol (*X*) and 3-[4-(2-hydroxypropyl)-1-piperazinyl]-1-propanol (*XI*), with *VI* and *XI* predominating. When the hydroboration was performed with sodium borohydride and boron trifluoride etherate at 20°C, the mixtures contained also compounds with allyl groups; in tetrahydrofuran the starting compound *I* predominated (irrespective of the reaction time) although this method is suitable for hydroboration of non-nitrogen alkenes[14]. In addition to the compound *I*, we identified 1-(4-allyl-1-piperazinyl)-2-propanol (*XII*), 3-(4-allyl-1-piperazinyl)-1-propanol (*XIII*), 1,4-bis(2-hydroxypropyl)piperazine (*XIV*), and the diol *XI*. Hydroboration in tetrahydrofuran afforded only very small amounts of the diols *XI* and *XIV*.

Composition of mixtures obtained by hydroboration with sodium borohydride and boron trifluoride etherate in diglyme at 150°C, followed by hydrolysis and oxidation, was independent of the heating time (the first sample was withdrawn after 15

minutes at 150°C). All the samples contained the alcohols *VIII* and *IX* and smaller amounts of the diols *XI* and *XIV* (Table I).

The obtained results are rationalized by Scheme 1. Since in the hydroboration of *I* with triethylamine-borane a part of the reagent was recovered, the reagent molecule can obviously react with more than one allyl group. The BH_3 species can add to the double bond as well as bind to the lone electron pair of the substrate nitrogen atom. Since the hydroboration with triethylamine-borane is performed at a temperature at which amine-boranes dissociate, this reaction is substantially less important than in hydroborations at 20°C and the boron atom is bonded preferentially in the γ-position relative to nitrogen. Consequently, the final product contains more 3-hydroxypropyl than 2-hydroxypropyl derivatives.

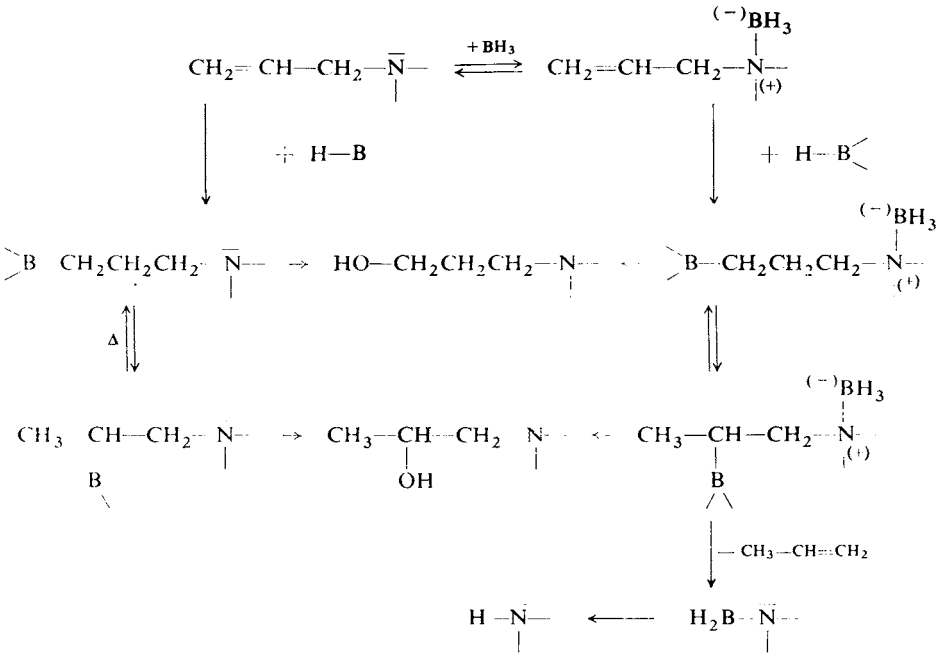
Since at 20°C the formation of amine-borane is faster than hydroboration, the products contain compounds with allyl group (*I*, *XII* and *XIII*). The fact that hydroboration in tetrahydrofuran gives mixtures containing substantially greater amount of the starting compound *I* than hydroboration in diglyme is caused by greater ability of tetrahydrofuran to form a complex with the borane. In hydroboration of an allyl attached to a BH_3-bonded nitrogen, the negative inductive effect of the nitrogen atom directs the boron atom preferentially into the β-position and the product thus contains a greater proportion of the 2-hydroxypropyl than 3-hydroxypropyl derivatives.

TABLE I

Products of hydrolysis and oxidation of hydroboration mixtures from compound *I* (%)

Compound	Hydroboration method[a]			
	A	*B*	*C*	*D*
I	0	75·5	15·7	0
VI	58·4	0	0	0
VII	8·0	0	0	0
VIII	6·0	0	0	47·0
IX	1·3	0	0	40·6
X	2·1	0	0	0
XI	24·2	0·1	16·4	8·9
XII	0	16·1	40·9	0
XIII	0	8·1	10·1	0
XIV	0	0·2	16·9	3·5

[a] A, triethylamine-borane; B, $NaBH_4 + BF_3.(C_2H_5)_2O$ in tetrahydrofuran; C, $NaBH_4 + BF_3.(C_2H_5)_2O$ in diglyme at 20°C; D, $NaBH_4 + BF_3.(C_2H_5)_2O$ in diglyme at 20°C followed by heating the hydroboration product to 150°C.



SCHEME 1

Organoboranes containing electronegative groups in the β-position undergo elimination reactions[15,16]. In some cases, such reactions are uncatalysed but often they require an acid or basic catalyst[15,16]. The alcohols *VIII* and *IX*, present in mixtures obtained by hydroboration with triethylamine-borane or diborane *in situ* in hot diglyme, are formed by elimination reactions. The absence of the starting compound *I* and alcohols *XII* and *XIII* in the last-mentioned mixture shows that at elevated temperatures the allyl groups are hydroborated with borane molecules which were coordinatively bonded to nitrogen atoms. Since the amount of the 2-hydroxypropyl derivatives (*IX*, *XI* and *XIV*) did not decrease on further heating, not all groupings with boron atom in β-position to nitrogen were able to eliminate. This indicates that the elimination occurs only if the nitrogen atom is coordinatively linked to borane which, as a Lewis acid, catalyses the reaction.

It is very probable that either the hydroboration with triethylamine-borane or heating the hydroboration product in diglyme involves also sigmatropic transfer of boron atoms along the carbon chain, characteristic for organoboranes[17,18].

EXPERIMENTAL

Temperature data are uncorrected. Gas–liquid chromatography was performed on a Chrom 5 chromatograph with CI-100 integrator (Laboratory Equipments, Prague), using 2 500 × 3 mm

glass columns packed with 3% OV-225 on Chromaton N-AW-DMCS, particles 0·125–0·16 mm (on-column injection, carrier gas nitrogen, flow rate 30 ml/min, programmed temperature 80–260°C 5°C/min, sample chamber temperature 240°C, samples 2–6 μl, flame ionizing detector temperature 260°C, hydrogen flow rate 40 ml/min, air flow-rate 500 ml/min). Relative responses of the compounds were not determined and were taken as equal. Mass spectra were measured on a Gas Chromatograph-Mass Spectrometer LKB 9000 (AB Stockholm) at 70 eV after separation of the compounds by gas–liquid chromatography under the above-described conditions (carrier gas helium). Infrared spectra were taken on a Perkin–Elmer 325 spectrophotometer. ^{1}H NMR spectra were measured on Varian XL-100-15 (100·1 MHz) or Tesla BS-567 (100·1 MHz) instruments at 35°C in deuteriochloroform and deuterium oxide with tetramethylsilane and sodium 4,4-dimethyl-4-silapentane-1-sulfonate, respectively, as internal standards. ^{11}B NMR spectra were obtained with the former instrument (at 32·1 MHz) at 35°C with trimethyl borate as internal standard. In all the NMR spectra the chemical shifts downfield from the standard are denoted as positive, in the ^{11}B NMR spectra the chemical shifts are calculated for boron trifluoride etherate as standard by adding 18·1 ppm. Dipole moments were measured at 1 MHz in benzene solutions, densities of the solutions were obtained in an Ostwald–Sprengel pycnometer. The dipole moment measurements were evaluated by the Halverstadt–Kumler method[19]. The atomic polarization increment was estimated to be 5% or 15% of the molar refraction calculated from the increments. Accuracy of the measurements was ±0·05 D.

Hydroboration of 1,4-Diallylpiperazine (*I*) with Triethylamine-borane

A mixture of compound *I* (12·7 g; 76 mmol) and triethylamine-borane[20] (17·5 g; 150 mmol) was heated under reflux condenser in a nitrogen atmosphere. When the bath temperature reached 120°C and a reaction commenced (vigorous boiling), the bath was removed and the mixture cooled. After the reaction had ended, triethylamine (13·4 g; 87%) was distilled off under nitrogen. The residue was cooled to afford a colourless transparent solid.

1,4-Bis(3-diethoxyborylpropyl)piperazine (*IV*)

Ethanol (20 ml) was added to the hydroboration product from the preceding experiment and the mixture which evolved hydrogen was set aside for 20 h. From the thus-obtained solution ethanol was removed by distillation *in vacuo* and the product was three times distilled affording 3·7 g (13%) of *IV*, b.p. 120–123°C/2·0 Pa. For $C_{18}H_{40}B_2N_2O_4$ (370·2) calculated: 58·40% C, 10·89% H, 5·85% B, 7·57% N; found: 58·10% C, 11·07% H, 5·67% B, 7·69% N. ^{1}H NMR spectrum (C^2HCl_3), ppm: 0·73 (4 H, t, J = 8 Hz), 2 CH_2—B; 1·17 (12 H, t, J = 7 Hz) 4 CH_3; 1·58 (4 H, m, $J_{\alpha,\beta} = J_{\beta,\gamma}$ = 8 Hz) 2 C—CH_2—C; 2·32 (4 H, t, J = 8 Hz) 2 N—CH_2—C—C—B; 2·48 (8 H, m) N(CH_2CH_2)$_2$N; 3·84 (8 H, q, J = 7 Hz) 4 O—CH_2. ^{11}B NMR spectrum (C^2HCl_3), ppm: +29·3 (s). Mass spectrum, *m/z* (relative intensities %): 370 (4), 241 (82), 142 (30), 101 (31), 73 (45), 45 (100).

5,8-Diaza-1,9-diboradispiro[4,2,4,2]tetradecane (*II*)

A) The crude hydroboration product (20·4 g), obtained from compound *I* (16·6 g; 100 mmol) and triethylamine-borane[20] (23·0 g; 200 mmol) as described above, was three times crystallized from benzene–cyclohexane to give 0·7 g (3·6%) of *II*, m.p. 157–180°C, uniform according to thin-layer chromatography (Silufol, benzene, R_F 0·6; Alufol, benzene, R_F 0·8). For $C_{10}H_{24}B_2N_2$ (194·0) calculated: 61·93% C, 12·47% H, 11·16% B, 14·44% N; found: 62·08% C, 12·53% H, 11·37% B, 14·45% N. ^{1}H NMR spectrum (C^2HCl_3), ppm: 0·56–1·02 (4 H, m) 2 CH_2—B; 1·80 (4 H, m, $J_{2,3} = J_{3,4} = J_{10,11} = J_{11,12}$ = 7 Hz) 2 C—CH_2—C; 2·67–3·60 (12 H, m)

CH_2—$N(CH_2CH_2)_2N$—CH_2. IR spectrum ($CHCl_3$), cm^{-1}: $\delta(BH_2)$ 1 190 (m); $\delta(CH_2)$ 1 437 (sh), 1 450 (s), 1 458 (m), 1 470 (m); $\nu(BH_2)$ 2 205 (w), 2 270 (sh), 2 305 (s), 2 330 (sh), 2 370 (sh), 2 390 (sh); $\nu(CH_2)$ 2 845 (m), 2 870 (m), 2 900 (sh), 2 940 (s), 2 950 (sh), 3 010 (m). μ_5 = 0·98 D, μ_{15} = 0·82 D.

B) The product obtained from *I* (5·0 g; 30 mmol) and triethylamine-borane[20] (6·9 g; 60 mmol) was distilled in a Hickman flask *in vacuo*, affording 1·4 g (20%) of triethylamine-borane, b.p. 85–89°C/0·2 kPa, identified by thin-layer chromatography (Alufol, benzene, R_F 0·7) and gas–liquid chromatography (10% E 301 on Chromaton N-AW-DMCS, 100°C).

The residue was then subjected to "flask to flask" distillation at 9 Pa and bath temperature 200–280°C which afforded 3·4 g of a white viscous product. The colourless distillation residue solidified on cooling below 250°C and did not melt again by heating to 280°C. Repeated crystallization of the distillate from benzene–cyclohexane gave 0·95 g (16%) of the title compound *II*, m.p. 160–185°C, identical (TLC and ^{1}H NMR spectrum) with the product obtained under *A*).

Hydrolysis and Oxidation of Hydroboration Product from Compound *I* and Triethylamine-borane

A) The hydroboration product (13·2 g) obtained from compound *I* (10·0 g; 60 mmol) and triethylamine-borane[20] (13·8 g; 120 mmol) was dissolved in acetone (120 ml). Hydrochloric acid (15%, 72 ml) was added dropwise to the stirred solution. The reaction mixture warmed spontaneously with evolution of hydrogen and was stirred under reflux for 15 min. Acetone and the excess acid were distilled off *in vacuo* and the residue was suspended in tetrahydrofuran (120 ml). Addition of 40% sodium hydroxide (34 ml) to the stirred suspension, followed by dropwise addition of 30% hydrogen peroxide (25 ml), resulted in an exothermic reaction. After refluxing for 3 h, the organic layer was separated and the aqueous one extracted with chloroform (4 × 30 ml). During 1 h the original organic layer deposited 3·4 g of a compound, m.p. 138–142°C, identified by ^{1}H NMR spectrum[4] as *VI*. The mother liquors after evaporation of tetrahydrofuran and standing overnight furnished another portion of *VI* (1·9 g after washing with methanol). The chloroform extract on evaporation *in vacuo* gave further *VI* (0·3 g after washing with methanol). The total yield was 5·6 g (46%); reported[21] m.p. 139–141°C.

The filtrates after washing the alcohol *VI* were combined, taken down and distilled, affording 3·2 g of semi-solid distillate, b.p. 75–130°C/2·7 Pa. The liquid portion (1·7 g) was redistilled at 75–88°C/4 Pa (1·1 g). A part (0·73 g) of this distillate was chromatographed on a column of silica gel (Silpearl) using benzene–2-propanol–ammonium hydroxide (10 : 5 : 1) as eluent. The first fractions contained two compounds (R_F = 0·3 and 0·5, Silufol, the same solvent system) which were shown by ^{1}H NMR spectrum[4] to be *VII* contaminated with *X*. Further elution afforded a product (R_F 0·1, Silufol, the same solvent system), b.p. 70°C/2 Pa, which, according to ^{1}H NMR spectrum[4], contained 70% of *VIII* and 30% of *IX*. For $C_7H_{16}N_2O$ (144·2) calculated: 58·30% C, 11·18% H, 19·30% N; found: 58·15% C, 11·32% H, 18·95% N.

B) The hydroboration product from *I* (2·0 g; 12 mmol) and triethylamine-borane[20] (2·8 g; 24 mmol) was hydrolyzed with hydrochloric acid in acetone as described in the preceding paragraph. After removal of acetone and excess acid by distillation, the residue was dissolved in water (19 ml) and tetrahydrofuran (24 ml). Half of the solution was made alkaline with 3M-NaOH (8·5 ml) and oxidized by dropwise addition of 30% hydrogen peroxide (1·6 ml). After stirring for 1 h at room temperature, the mixture was saturated with potassium carbonate, the organic layer was separated and the aqueous one repeatedly extracted twice with 2-propanol (2 × 12 ml). The extracts were added to the original organic layer and this solution was analyzed by gas–liquid chromatography and mass spectrometry (Table I).

Hydroboration of Compound *I* with Sodium Borohydride and Boron Trifluoride Etherate

A) Boron trifluoride etherate (3·6 ml; 28 mmol) was added at 25°C during 45 min in a nitrogen atmosphere to a stirred mixture of sodium borohydride (0·8 g; 20 mmol), compound *I* (1·7 g; 10 mmol) and tetrahydrofuran (25 ml). The mixture was stirred for 1—2 h, decomposed by dropwise addition of 15% HCl (5·0 ml) and the stirring was continued until the hydrogen evolution ceased completely. After addition of 40% NaOH (4·5 ml) and 30% hydrogen peroxide (4·0 ml) the mixture was refluxed with stirring for 1 h and saturated with potassium carbonate. The organic layer was separated, the aqueous one extracted with 2-propanol (3 × 5 ml), the extracts were combined with the original organic layer and analyzed by gas–liquid chromatography and mass spectrometry (Table I).

B) A solution of boron trifluoride etherate (1·8 ml; 14 mmol) in diglyme (3·5 ml) was added dropwise over 15 min to a stirred mixture of compound *I* (0·8 g; 5 mmol), sodium borohydride (0·4 g; 10 mmol) and diglyme (15 ml) at 20°C under nitrogen. After stirring at 20°C for 1 h, a 2 ml sample was withdrawn, the mixture was heated to 150°C during 15 min and kept at this temperature. Further samples were taken 0·25 h, 1·25 h, 2·25 h and 3·0 h after the constant temperature had been achieved. Each sample was immediately decomposed with 15% HCl (0·8 ml), mixed with 40% NaOH (1·0 ml), tetrahydrofuran (2·0 ml) and 30% hydrogen peroxide (0·7 ml) and refluxed with stirring for 1 h. The mixture was saturated with potassium carbonate, the organic layer separated, the aqueous one extracted with 2-propanol (2 × 1 ml) and the extract combined with the original organic layer. The solutions were analyzed by gas–liquid chromatography and mass spectrometry and their composition was shown to be independent of the heating time. The results are given in Table I.

1,4-Diallylpiperazine Dihydrochloride

Hydrochloric acid (15%; 120 ml) was added with stirring and cooling to compound *I* (35·9 g; 216 mmol). After evaporation to dryness, the residue was crystallized from ethanol to give 48·0 g (93%) of the dihydrochloride, m.p. 255—265°C (decomposition). For $C_{10}H_{20}Cl_2N_2$ (239·2) calculated: 50·21% C, 8·43% H, 29·65% Cl, 11·71% N; found: 50·20% C, 8·44% H, 29·55% Cl, 11·62% N. ^{1}H NMR spectrum (^2H_2O), ppm: 3·66 (8 H, bs) $N(CH_2CH_2)_2N$; 3·89 (4 H, d, J = = 7 Hz) 2 N—CH_2—C=; 5·50—6·20 (6 H, m) 2 CH=CH_2.

1,4-Diallylpiperazine-diborane (*V*)

Water (55 ml) was added dropwise in the course of 45 min to a stirred suspension of 1,4-diallylpiperazine dihydrochloride (22·6 g; 94 mmol) and sodium borohydride (8·9 g; 240 mmol) in diethyl ether (250 ml). After stirring for 30 min, the mixture was filtered and the ethereal layer separated. The solid on the filter almost completely dissolved on washing with tetrahydrofuran (4 × 25 ml) and the washings were combined with the ethereal layer. The formed white suspension was homogenized by addition of tetrahydrofuran (50 ml), the solution was dried over potassium carbonate and taken down *in vacuo*. The residue after washing with diethyl ether afforded 8·1 g of product, m.p. 110—112°C (decomposition from 100°C). Thin-layer chromatography (Alufol, benzene, developed with iodine vapours): 3 spots (R_F 0, 0·2 and 0·7) of which neither corresponded to *I* or *II*. Crystallization from benzene–cyclohexane afforded 3·2 g (17%) of the product *V*, m.p. 110—112°C, homogeneous according to TLC (R_F 0·7). For $C_{10}H_{24}B_2N_2$ (194·0) calculated: 61·93% C, 12·47% H, 11·16% B, 14·44% N; found: 61·71% C, 12·26% H, 11·10% B, 14·34% N. ^{1}H NMR spectrum (C^2HCl_3), ppm: 2·43—3·20 (4 H, m) 2 CH_2—C=; 3·30—3·90 (8 H, m) $N(CH_2CH_2)_2N$; 5·16—5·64 (4 H, m) 2 =CH_2; 5·98—6·53 (2 H, m) 2 —CH=. ^{11}B NMR

spectrum (C^2HCl_3), ppm: −13·4 (d, J = 75 Hz). IR spectrum (KBr), cm^{-1}: γ(CH) 909 (m), 990 (s); ν(BN) 1 000 (s), 1 165 (s); $\delta(BH_3)$ 1 190 (s); δ(CH, CH_2) 1 428 (s), 1 445 (m), 1 450 (m), 1 460 (s); ν(C=C) 1 646 (w); $\nu(BH_3)$ 2 290 (s), 2 340 (s), 2 400 (s), 2 420 (sh); $\nu(CH_2)$ 2 930 (sh), 2 940 (m), 2 960 (m); $\nu(=CH_2)$ 2 995 (m), 3 090 (w); ν(=CH—) 3 040 (w).

Elemental analyses were performed in the Analytical Laboratory of our Department (Dr L. Helešic, Head). NMR *spectra were measured in the Laboratory of* NMR *Spectroscopy (Dr P. Trška, Head),* IR *spectra were recorded by Dr A. Kohoutová and Dr E. Janečková in the Laboratory of Absorption Spectroscopy. Mass spectra were taken by Dr J. Mitera and Dr I. Víden, Laboratory of Mass Spectrometry. Quantitative gas–liquid chromatographic analyses were performed by Dr F. Pudil, Department of Food Chemistry and Analysis. The authors are indebted also to Dr V. Jehlička, Department of Physical Chemistry, for the dipole moment determinations.*

REFERENCES

1. Ferles M., Kafka S.: This Journal *47*, 2150 (1982).
2. Ferles M., Kafka S.: This Journal *48*, 1068 (1983).
3. Kafka S., Ferles M.: This Journal *49*, 78 (1984).
4. Kafka S., Čermák J., Novák T., Pudil F., Víden I., Ferles M.: This Journal *50*, 1201 (1985).
5. Polívka Z., Kubelka V., Holubová N., Ferles M.: This Journal *35*, 1131 (1970).
6. Onak T.: *Organoborane Chemistry*, p. 191. Academic Press, New York 1975.
7. Bax C. M., Katritzky A. R., Sutton L. E.: J. Chem. Soc. *1958*, 1258.
8. Mostovoi N. V., Dorokhov V. A., Mikhailov B. M.: Izv. Akad. Nauk SSSR, Ser. Khim. *1966*, 90.
9. Ferles M., Polívka Z.: This Journal *33*, 2121 (1968).
10. Polívka Z.: *Thesis*. Prague Institute of Chemical Technology 1969.
11. Philips W. D., Miller H. C., Muetterties E. L.: J. Amer. Chem. Soc. *81*, 4496 (1959).
12. Nöth H., Vahrenkamp H.: Chem. Ber. *99*, 1049 (1966).
13. Mancilla T., Santiesteban F., Contreras R., Klaébé A.: Tetrahedron Lett. *1982*, 1561.
14. Brown H. C.: *Organic Syntheses* via *Boranes*, p. 17. Wiley, New York 1974.
15. Mikhailov B. M., Bubnov Yu. N.: *Bororganicheskie Soedineniya v Organicheskom Sinteze*, p. 98. Nauka, Moscow 1977.
16. Zaidlewicz M.: *Comprehensive Organometallic Chemistry* (G. Wilkinson, Ed.), Vol. 7, p. 235. Pergamon Press, Oxford 1983.
17. Ref.[15], p. 164.
18. Brown H. C.: Ref.[16], p. 119.
19. Halverstadt I. F., Kumler W. D.: J. Amer. Chem. Soc. *64*, 2988 (1942).
20. U.S. Borax Corporation: Brit. 952 811 (1964); Chem. Abstr. *61*, 2970 (1964).
21. Paul K., Blanton C. D., jr: J. Med. Chem. *16*, 1391 (1973).

Translated by M. Tichý.