HYDROBORATION OF 1-(3-BUTENYL)PIPERIDINE AND 1-(4-PENTENYL) PIPERIDINE*

Stanislav KAFKA and Miloslav FERLES

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

Received October 8th, 1982

Dedicated to the Academician O. Wichterle on the occasion of his 70th birthday.

Hydroboration of 1-(3-butenyl)- (*Ia*) and 1-(4-pentenyl)piperidine (*Ib*) with triethylamine-borane followed by hydrolysis and oxidation afforded the appropriate alcohols *IIIc* and *IIIf* resp. The spirocyclic amine-borane *IIa,b* isolated from the hydroboration products were transformed by hydrochloric acid into the hydrochlorides of piperidinealkylboronic acids *IVa,b* which were oxidized in an alkaline medium with hydrogen peroxide to the primary alcohols *IIIc,f*. Diethyl ester *V* was prepared by ethanolysis of *IIa*.

This work is a continuation of our previous communication[1] dealing with the hydroboration of N-allyl derivatives of pyrrolidine, piperidine, hexahydroazepine and morpholine. The topic of this study is the hydroboration of N-alkenylpiperidines containing an alkyl chain longer than that of allyl.

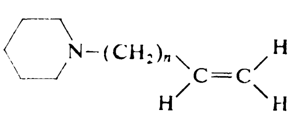
Hydroboration of 1-(3-butenyl)- (*Ia*) and of 1-(4-pentenyl)-piperidine (*Ib*) with triethylamine-borane proceeds similarly to that of N-allylamines affording analogous spirocyclic amine-boranes, *i.e.* 6-aza-1-bora-spiro[5,5]undecane (*IIa*) and 6-aza-7-boraspiro[5,6]dodecane (*IIb*) respectively. The spirocyclic structure of these compounds was deduced on the ground of similar evidences as presented in paper[1].

The infrared spectra of compounds *IIa,b* show again the absorption bands corresponding to the valence vibrations (in the region 2 220 – 2 400 cm^{-1}) and to the deformation vibrations (in the region 1 120 – 1 200 cm^{-1}) of the B—H bonds. In the ^1H NMR spectra of compounds *IIa,b* the signals of methylene groups bound to the N-atom are shifted to the lower magnetic field compared to the corresponding methylene groups of the alcohols *IIIa – IIIf*. In the ^{11}B NMR spectra of compounds *IIa,b* the characteristic BH_2 triplets show also interaction constants near to 100 Hz and chemical shifts of about – 10 ppm (referred to $BF_3.O(C_2H_5)_2$). Finally, the mass spectra exhibit again the less intensive molecular ions and the intensive $(M-1)^+$ ions. All these evidences were discussed in detail in the previous paper of this series[2].

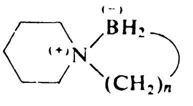
---

* Part XV in the series Hydroboration of Unsaturated Amines; Part XIV: This Journal *48*, 1068 (1983).

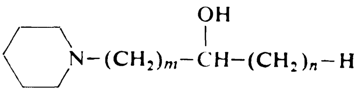
The amine-boranes *IIa,b* were transformed by hydrochloric acid into the hydrochlorides of the boronic acids *IVa,b*. These hydrochlorides were oxidized with hydrogen peroxide in the presence of sodium hydroxide to the primary piperidine alcohols *IIIc,f* free of secondary alcohols *IIIa,b* and *IIId,e* resp. We also tried the direct oxidation of the amine-borane *IIa* with hydrogen peroxide in the presence of sodium hydroxide. In contrast to boranes which are not stabilized by the intramolecular bond B – N and with which the above oxidation is commonly used in the preparation of alcohols[3], the amine-borane *IIa* was found unchanged. Such a resistance to the oxidation with hydrogen peroxide in an alkaline medium was observed already earlier at 1,1-dimethylperhydro-1,2-azaborine[4]. The ethanolysis of the amine-borane *IIa* proceeds only reluctantly. A complete decomposition of this compound needs boiling for 4 hours in ethanol. In this way, the diethyl ester of 4-(1-piperidyl)butylboronic acid (*V*) was prepared.



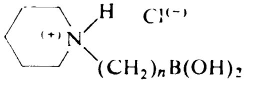
I



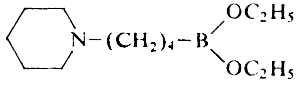
II



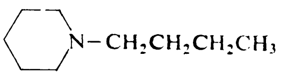
III



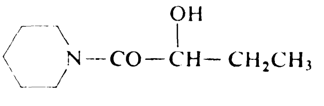
IV



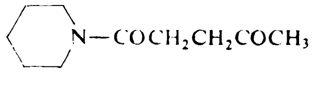
V



VI



VII



VIII

In formula *I*: *a*, $n = 2$; *b*, $n = 3$. In formulae *II*, *IV*: *a*, $n = 4$; *b*, $n = 5$. In formula *III*: *a*, $m = 1$, $n = 2$; *b*, $m = 2$, $n = 1$; *c*, $m = 3$, $n = 0$; *d*, $m = 2$, $n = 2$; *e*, $m = 3$, $n = 1$; *f*, $m = 4$, $n = 0$.

1-(3-Butenyl)piperidine (*Ia*) and 1-(4-pentenyl)piperidine (*Ib*) were also hydroborated with triethylamine-borane and the products of hydroboration were hydrolyzed with hydrochloric acid and then oxidized with hydrogen peroxide. In both cases, a product containing mainly primary alcohol (79% with *Ia* and approximately the same amount with *Ib*) was obtained, accompanied with a secondary alcohol having the hydroxylic group bound in the position corresponding to the addition of water according to the Markownikoff rule to *IIIb* and *IIIe* resp. Alcohols *IIIa* and *IIIb* with the hydroxylic group remoted by one more C-atom from the end of the chain can be present in these products only in trace amounts. In the product obtained from *Ia,* also 1-butylpiperidine (*VI*) was identified by means of gas-liquid chromatography combined with mass spectrometry.

EXPERIMENTAL

The temperature data are not corrected. The gas–liquid chromatography was carried out on the Chrom-2 instrument (columns 170 cm × 6 mm) or on the Chrom-5 instrument (columns 250 cm× × 3 mm). The used column packings were 15% butandiolsuccinate (BDS) or 15% silicone elastomer E 301 on the Chromosorb N-AW support or 15% Carbowax 20M on the Chromaton N-AW-HMDS support with the Chrom-2 equipment, and 10% silicone elastomer E 301 or 15% Carbowax 20M on the Chromaton N-AW-DMCS support with the Chrom-5 instrument. The used chromatograph, the stationary phase and the temperature are mentioned separatedly for each case. The infrared spectra were obtained with a Perkin–Elmer Spectrophotometer, Model 325. The NMR spectra were recorded at 35°C using a Varian XL-100-15 Spectrometer (^{1}H at 100·1 MHz, ^{11}B at 32·1 MHz). The ^{1}H chemical shifts are referred to tetramethylsilane in deuteriochloroform or to sodium 4,4-dimethyl-4-silapentan-1-sulfonate in deuterium oxide (internal standards). The ^{11}B NMR spectra were measured in deuteriochloroform in the presence of $B(OCH_3)_3$ ($\delta = 18{\cdot}1$ ppm); the chemical shifts are referred to $BF_3.O(C_2H_5)_2$ ($\delta = 0$ ppm). In the description of spectra, the individual positions in the piperidine ring are designated by numbers, those in the side chain are denoted by Greek letters. The mass spectra were measured with a Gas Chromatograph-Mass Spectrometer LKB 9000, Produkter AB Stockholm. The ion species are given in the *m*/*z* units.

1-(3-Butenyl)piperidine (*Ia*)

To a stirred mixture of potassium carbonate (63·1 g, 0·46 mol), of piperidine (35·3 g, 0·42 mol) and of 104 ml of 2-butanone was added the solution of 3-butenyl bromide[5] (56·0 g, 0·42 mol) in 42 ml of 2-butanone. The mixture was refluxed for 7 hours under stirring. The cooled reaction mixture was filtered, the solvent was removed by the column distillation and the residue was distilled at 0·101 MPa (761 Torr) yielding 48·5 g (84%) of *Ia* which had b.p. 160–167°C and was pure according to GLC (Chrom-2, E 301, 130°C). Allan and Swan[6] report b.p. 152°C. The ^{1}H NMR spectrum (C^2HCl_3, ppm): 1·30–1·76 (6 H, m) H in the positions 3, 4 and 5; 2·08 to 2·56 (8 H, m) H in the positions 2,6, α and β; 5·01 (1 H, m, $J_{gem} = 1$ Hz, $J_{\gamma,\delta'} = 18$ Hz) H in the position δ′; 5·04 (1 H, m, $J_{gem} = 1$ Hz, $J_{\gamma,\delta} = 9$ Hz) H in the position δ; 5·79 (1 H, m, $J_{\beta,\gamma} = 7$ Hz, $J_{\gamma,\delta} = 9$ Hz, $J_{\gamma,\delta'} = 18$ Hz) H in the position γ. The infrared spectrum (CCl_4, cm^{-1}): 1 445 (s) $\delta(CH_2)$, 1 455 (s) $\delta(CH_2)$, 1 470 (s) $\delta(CH_2)$, 1 645 (s) $\nu(C{=}C)$, 2 760 (s) $\nu(CH_2)$, 2 800 (s) $\nu(CH_2)$, 2 860 (s) $\nu(CH_2)$, 2 940 (s) $\nu(CH_2)$, 2990 (s) ν (${=}CH_2$), 3 005 (s) $\nu({=}CH{-})$, 3 090 (s) $\nu({=}CH_2)$.

Hydroboration of 1-(3-Butenyl)piperidine (*Ia*)

A mixture of *Ia* (22·3 g, 0·16 mol) and of $(C_2H_5)_3N.BH_3$ (18·4 g, 0·16 mol, ref.[7]) was heated under reflux condenser in a nitrogen atmosphere. At 125°C (bath) when a vivid reaction started bringing the mixture to boil, the bath was taken away. After the reaction ceased, the mixture was cooled down and the liquid, identified by GLC (Chrom-2, E 301 or BDS, 80°C) as triethylamine, was distilled off. The remainder amounted to 27·1 g of crude product. To the solution of 2·0 g of this crude hydroboration product in 13 ml of acetone was added dropwise 8 ml of 15% HCl under stirring. The reaction was accompanied by an evolution of gas and by a spontaneous heating to boil. The mixture was refluxed for 15 min under stirring after which acetone and the excess acid were distilled off *in vacuo*. The solid residue was dissolved in 10·5 ml of water and 13 ml of tetrahydrofuran, and subsequently 9·0 ml of 3M-NaOH and 1·7 ml of 30% H_2O_2 were added (spontaneous heating of the mixture). After 1 hour boiling under stirring the mixture was cooled down and saturated with K_2CO_3, the organic layer was separated and the aqueous layer was extracted with ether (4 × 7 ml). The extracts were combined with the original organic layer, the whole solution was dried with K_2CO_3 and the solvents were removed by distillation, leaving 1·4 g of a colorless liquid, b.p. 95—110°C/1·6 kPa (12 Torr). By means of GLC (Chrom-5, Carbowax 20 M, 200°C) it was found that the product contained 79% of *IIIc*, 18% of *IIIb* and traces of *IIIa* but no starting compound *Ia*. The quantitative determination was performed by the internal standard method (*IIIe* in this case). In addition, the mass spectrometry combined with gas-liquid chromatography revealed 1-butylpiperidine (*VI*) in the product. The ^1H NMR spectrum as well as the infrared spectrum show only the signals present in the spectra of *IIIc* and *IIIb*. The mass spectrum of *VI* (70 eV): 141 (4%, M^+), 98 (100%).

6-Aza-1-boraspiro[5,5]undecane (*IIa*)

The crude product from the hydroboration of *Ia* (25·1 g) was first deliberated of 4·2 g of the fraction of b.p. 110—133°C/1·7 kPa (13 Torr) by the column distillation and the remainder was then distilled in a distilling collar apparatus giving subsequently 15·4 g of a main fraction boiling in the range of 90—130°C/5 Pa (0·04 Torr) (the greatest part distilled near the lower temperature of this interval) and 1·8 g of a viscous distillation residue. A repeated distillation of the main fraction yielded 10·7 g (47%) of compound *IIa*, b.p. 131—133°C/1·6 kPa (12 Torr). For $C_9H_{20}BN$ (153·1) calculated: 70·61% C, 13·17% H, 7·07% B, 9·15% N; found: 70·63% C, 12·95% H, 7·55% B, 9·21% N. The ^1H NMR spectrum (C^2HCl_3, ppm): 0·45 (2 H, m) H in the position 2; 1·32—1·93 (10 H, m) H in the positions 3,4, 8,9 and 10; 2·55—3·13 (6 H, m) H in the positions 5,7 and 11. The ^{11}B NMR spectrum (C^2HCl_3): −11·3 (t, $J = 91$ Hz). The infrared spectrum (CCl_4, cm^{-1}): 1 120 (s) $\delta(BH_2)$, 1 130 (s) $\delta(BH_2)$, 1 146 (s) $\delta(BH_2)$, 1 163 (m) $\delta(BH_2)$, 1 180 (s) $\delta(BH_2)$, 1 450 (s) $\delta(CH_2)$, 1 455 (m) $\delta(CH_2)$, 1 465 (m) $\delta(CH_2)$, 2 220 (m) $\nu(BH_2)$, 2 250 (m) $\nu(BH_2)$, 2 280 (i) $\nu(BH_2)$, 2 300 (s) $\nu(BH_2)$, 2 350 (i) $\nu(BH_2)$, 2 370 (i) $\nu(BH_2)$, 2 390 (i) $\nu(BH_2)$, 2 820 (m) $\nu(CH_2)$, 2 860 (s) $\nu(CH_2)$, 2 910 (i) $\nu(CH_2)$, 2 930 (s) $\nu(CH_2)$, 2 970 (i) $\nu(CH_2)$, 3 000 (i) $\nu(CH_2)$. The mass spectrum: 152 (100%, $M^+ - 1$), 151 (30%), 98 (35%), 96 (43%).

The foregoing low-boiling fraction (2·3 g) and the distillation residue (1·8 g) were hydrolyzed and oxidized in the same manner as mentioned above. For 1 mmol of the substrate it was used: 1 ml of acetone, 0·6 ml of 15% HCl, 0·8 ml of water, 1 ml of tetrahydrofuran, 0·7 ml of 3M-NaOH, 0·13 ml of 30% H_2O_2 and 4 × 0·5 ml of diethyl ether (taking the molecular mass of substrates equal to the molecular mass of compound *IIa*). Mixtures of compounds were obtained (1·8 g from the low-boiling fraction, 1·2 g from the distillation residue) which were according to GLC similar to mixtures obtained in the analogous working up of the crude hydroboration product. The proportion of *IIIb* obtained from the low-boiling fraction was somewhat higher and that from the distillation residue somewhat lower than that obtained from the rough hydroboration product.

Diethyl 4-(1-Piperidyl)butylboronate (*V*)

A solution of compound *IIa* (2·0 g, 0·013 mol) in ethanol was boiled till a gas evolved (4 hours). Ethanol was removed by distillation leaving 2·7 g (86%) of *V*, b.p. 123—125°C/1·7 kPa (13 Torr).

For $C_{13}H_{28}BNO_2$ (241·2) calculated: 64·74% C, 11·70% H, 4·48% B, 5·81% N; found: 64·45%C, 11·39% H, 4·52% B, 5·95% N. The ^1H NMR spectrum (C^2HCl_3, ppm): 0·75 (2 H, t, $J = 7·5$ Hz) H in the position δ; 1·17 (6 H, t, $J = 7$ Hz) 2 CH_3; 1·32—1·82 (10 H, m) H in the positions 3,4,5, β and γ; 2·18—2·82 (6 H, m) H in the positions 2,6 and α; 3·82 (4 H, q, $J = 7$ Hz) 2 OCH_2. The ^{11}B NMR spectrum (C^2HCl_3): +24·9 (s). The infrared spectrum (CCl_4, cm^{-1}): 723 (m), 1 037 (i), 1 046 (m), 1 100 (w), 1 117 (w), 1 150 (w), 1 180 (w), 1 220 (w), 1 242 (m), 1 260 (i), 1 270 (m), 1 320 (s), 1 335 (i), 1 345 (i), 1 367 (i), 1 373 (s), 1 395 (i), 1 410 (m), 1 425 (m), 1 443 (m), 1 450 (i), 1 470 (w), 1 485 (w), 2 740 (i), 2 770 (m), 2 810 (m), 2 860 (m) $\nu(CH_2)$, 2 920 (i) $\nu(CH_2)$, 2 940 (s) $\nu(CH_2)$, 2 980 (s) $\nu(CH_2)$.

Hydrochloride of 4-(1-Piperidyl)butylboronic Acid (*IVa*)

To the solution of 4·0 g (0·026 mol) of *IIa* in 26 ml of acetone was added dropwise 16 ml of 15% HCl under stirring (gas evolution, spontaneous heating to boil). The mixture was refluxed for 15 min under stirring, acetone and excess acid were distilled off and the residue was repeatedly crystallized from 2-propanol giving 3·5 g (61%) of *IVa* which melted at 125—127°C. Being further heated it again solidified and melted with decomposition at 225—240°C. For $C_9H_{21}BClNO_2$ (221·6) calculated: 48·79% C, 9·56% H, 4·88% B, 16·00% Cl, 6·32% N; found: 48·72% C, 9·72% H, 5·21% B, 16·29% Cl, 6·19% N. The ^1H NMR spectrum (^2H_2O, ppm): 0·81 (2 H, t, $J = 7·5$ Hz) H in the position δ; 1·26—2·13 (10 H, m) H in the positions 3,4,5, β and γ; 2·69—3·19 (4 H, m) and 3·50 (2 H, d, $J = 12$ Hz) H in the positions 2,6 and α. The infrared spectrum (KBr, cm^{-1}): 580 (w), 675 (w), 727 (m), 778 (w), 792 (i), 802 (m), 830 (w), 858 (w), 870 (w), 910 (w), 950 (w), 960 (m), 1 010 (s), 1 015 (i), 1 035 (w), 1 068 (w), 1 078 (w), 1 083 (i), 1 110 (w), 1 130 (i), 1 138 (m), 1 175 (w), 1 188 (m), 1 207 (m), 1 242 (w), 1 274 (m), 1 300 (w), 1 310 (i), 1 325 (m), 1 340 (m), 1 350 (i), 1 360 (s), 1 380 (s), 1 400 (i), 1 424 (m), 1 452 (s), 1 472 (m), 2 550 (s), 2 660 (s), 2 700 (s), 2 880 (m) $\nu(CH_2)$, 2 935 (s) $\nu(CH_2)$, 2 950 (s) $\nu(CH_2)$, 3 180 (s), 3 330 (s), 3 370 (s), 3 530 (s).

4-(1-Piperidyl)-1-butanol (*IIIc*)

To the solution of *IVa* (1·5 g, 0·0068 mol) in 5·4 ml of water and 6·8 ml of tetrahydrofuran was added 4·8 ml of 3M-NaOH and 0·9 ml of 30% H_2O_2 (spontaneous heating). After 1 hour stirring at room temperature the mixture was saturated with K_2CO_3, the organic layer was separated and the aqueous layer was extracted with four 3·5 ml portions of diethyl ether. The extracts and the organic layer were combined, dried with K_2CO_3, the solvents were evaporated and the residue was distilled yielding 1·0 g (94%) of *IIIc* which was pure according to GLC (Chrom-2, Carbowax 20M, 220°C) and had b.p. 110—112°C/1·6 kPa (12 Torr). Vejdělek and Trčka[8] report b.p. 122°C/1·6 kPa (12 Torr).

1-(4-Pentenyl)piperidine (*Ib*)

This compound was prepared analogously to its homologue *Ia* by the reaction of piperidine (17·0 g, 0·20 mol) with 5-pentenyl bromide[9]; (29·8 g, 0·20 mol) in the presence of K_2CO_3. The obtained *Ib* product (26·0 g, 85%) was pure according to GLC (Chrom-2, E 301, 170°C) and had b.p. 66—67·5°C/1·5 kPa (11 Torr); Glacet[10] gives b.p. 75°C/1·7 kPa (13 Torr). The ^1H NMR spectrum (C^2HCl_3, ppm): 1·22—1·80 (8 H, m) H in the positions 3,4,5, and β; 2·02 (2 H, t, $J =$ $= 7$ Hz) H in the position γ; 2·10—2·60 (6 H, m) H in the positions 2,6 and α; 4·99 (1 H, m, $J_{\delta,\varepsilon} = 9$ Hz) H in the position ε; 5·02 (1 H, m, $J_{\varepsilon,\varepsilon'} = 2$ Hz, $J_{\delta,\varepsilon'} = 17$ Hz) H in the position ε'; 5·88 (1 H, m, $J_{\gamma,\delta} = 7$ Hz, $J_{\delta,\varepsilon} = 9$ Hz, $J_{\delta,\varepsilon'} = 17$ Hz) H in the position δ. The infrared spectrum (CCl_4, cm^{-1}): 1 445 (s) $\delta(CH_2)$, 1 455 (s) $\delta(CH_2)$, 1 470 (s) $\delta(CH_2)$, 1 644 (s) $\nu(C{=}C)$, 2 760 (s) $\nu(CH_2)$, 2 805 (s) $\nu(CH_2)$, 2 860 (s) $\nu(CH_2)$, 2 940 (s) $\nu(CH_2)$, 2 980 (i) $\nu({=}CH_2)$, 3 000 (i) $\nu({=}CH{-})$, 3 085 (m) $\nu({=}CH_2)$.

6-Aza-7-boraspiro[5,6]dodecane (*IIb*)

The hydroboration of 1-(4-pentenyl)piperidine (*Ib*) (15·3 g, 0·1 mol) with triethylamine-borane[7] (11·5 g, 0·1 mol) was performed analogously to the hydroboration of *Ia*. A repeated distillation of the hydroboration product gave 6·4 g (38%) of *IIb*, b.p. 144—146°C/1·6 kPa (12 Torr). For $C_{10}H_{22}BN$ (167·1) calculated: 71·87% C, 13·27% H, 5·48% B, 8·38% N; found: 71·71% C, 13·16% H, 6·53% B, 8·21% N. The ^1H NMR spectrum (C^2HCl_3, ppm): 0·31—0·66 (2 H, m) H in the position 2; 1·36—2·01 (12 H, m) H in the positions 3,4,5,9,10 and 11; 2·56—3·22 (6 H, m) H in the positions 6,8, and 12. The ^{11}B NMR spectrum (C^2HCl_3, ppm): −9·3 (t, $J = 92$ Hz). The mass spectrum: 166 (100%, $M^+ - 1$), 165 (30%), 98 (68%), 96 (54%). The infrared spectrum (CCl_4, cm^{-1}): 1 132 (s) $\delta(BH_2)$, 1 150 (s) $\delta(BH_2)$, 1 165 (m) $\delta(BH_2)$, 1 176 (s) $\delta(BH_2)$, 1 190 (m) $\delta(BH_2)$, 1 450 (s) $\delta(CH_2)$, 1 470 (m) $\delta(CH_2)$, 2 240 (m) $\nu(BH_2)$, 2 260 (m) $\nu(BH_2)$, 2 305 (s) $\nu(BH_2)$, 2 340 (i) $\nu(BH_2)$, 2 360 (i) $\nu(BH_2)$, 2 400 (i) $\nu(BH_2)$, 2 800 (m) $\nu(CH_2)$, 2 860 (s) $\nu(CH_2)$, 2 930 (s) $\nu(CH_2)$.

Hydrochloride of 5-(1-Piperidyl)pentylboronic Acid (*IVb*)

The compound *IIb* (2·9 g, 0·017 mol), was hydrolyzed with 15% hydrochloric acid (10 ml) in acetone (17 ml) in the same way as in the preparation of the hydrochloride *IVa*. The yield was 3·0 g (74%) of the hydrochloride *IVb*, m.p. 122—124°C (2-propanol). For $C_{10}H_{23}BClNO_2$ (235·6) calculated: 50·99% C, 9·84% H, 4·59% B, 15·05% Cl, 5·95% N; found: 51·02% C, 10·11% H, 4·76% B, 14·77% Cl, 5·89% N. The ^1H NMR spectrum (^2H_2O, ppm): 0·78 (2 H, t, $J = 7$ Hz) H in the position ε; 1·20—1·50 (4 H, m) H in the positions γ and δ; 1·50—2·10 (8 H, m) H in the positions 3,4,5 and β; 2·68—3·18 (4 H, m) and 3·50 (2 H, d, $J = 12$ Hz) H in the positions 2,6 and α. The infrared spectrum (KBr, cm^{-1}): 724 (m), 746 (m), 755 (m), 777 (m), 800 (m), 815 (i), 858 (w), 904 (w), 936 (w), 950 (m), 958 (m), 1 012 (w), 1 024 (w), 1 035 (w), 1 052 (m), 1 066 (m), 1 085 (m), 1 102 (i), 1 118 (m), 1 128 (i), 1 142 (w), 1 181 (m), 1 189 (m), 1 206 (m), 1 260 (s), 1 268 (i), 1 288 (m), 1 305 (m), 1 318 (s), 1 352 (s), 1 365 (s), 1 382 (s), 1 410 (s), 1 435 (s), 1 458 (m), 1 469 (s), 1 483 (m), 1 590 (w), 1 625 (w), 2 170 (w), 2 810 (m), 2 865 (s) $\nu(CH_2)$, 2 900 (m) $\nu(CH_2)$, 2 950 (s) $\nu(CH_2)$, 3 000 (m), 3 070 (s), 3 160 (s), 3 240 (s), 3 380 (i).

5-(1-Piperidyl)-1-pentanol (*IIIf*)

Hydrochloride *IVb* (1·5 g, 0·0064 mol) was oxidized similarly as described in the preparation of *IIIc*. The obtained compound (0·85 g, 78%) *IIIf* was pure according to GLC (Chrom-5, Carbowax 20 M, 220°C) and had b.p. 127—129°C/1·7 kPa (13 Torr). Solovyev[11] reports b.p. 140°C/1·7 kPa (13 Torr).

The crude product of the hydroboration of *Ib* with triethylamine-borane (15·3 g, 0·1 mol) was hydrolyzed and oxidized in the same way as with the product prepared by the hydroboration of the compound *Ia*. The obtained mixture (14·7 g) exhibited according to GLC (Chrom-5, Carbowax 20 M, 220°C) prevailing amount of alcohol *IIIf* (82% of the area demarcated by all peaks) accompanied by alcohols *IIIe* and *IIId* (imperceptible peak).

1-(2-Hydroxybutanoyl)piperidine (*VII*)

The mixture of (±)-ethyl 2-hydroxybutanoate (6·5 g, 0·049 mol) and of piperidine (25·0 g 0·294 mol) was refluxed for 17 hours. According to GLC (Chrom-5, E 301, 140°C) practically all ester reacted. The excess piperidine was evaporated and the residue was repeatedly distilled yielding 4·1 g (49%) of liquid of b.p. 89—90°C/3 Pa (0·02 Torr), uniform according to GLC (E 301, 180°C) and identified as *VII*. For $C_9H_{17}NO_2$ (171·2) calculated: 63·13% C, 10·01% H, 8·18% N; found: 62·73% C, 10·22% H, 7·95% N. The ^{1}H NMR spectrum (C^2HCl_3, ppm): 1·00 (3 H, t, $J = 7$ Hz) H in the position δ; 1·27—1·99 (8 H, m) H in the positions 3,4,5 and γ; 3·35 (2 H, m) and 3·61 (2 H, m) H in the positions 2 and 6 (at 60°C these multiplets overlaps mutually); 4·15—4·50 (2 H, m) H in the position β and OH. The infrared spectrum (CCl_4, cm^{-1}): 1 648 (s) ν(CO), 2 870 (m) ν(CH_2), 2 950 (s) ν(CH_2), 3 450 (w) ν(OH).

1-(1-Piperidyl)-2-butanol (*IIIa*)

To the suspension of 70% $LiAlH_4$ (1·6 g, 0·030 mol) in 150 ml of diethyl ether was under stirring added a solution of *VII* (3·4 g, 0·020 mol) in 8 ml of diethyl ether in such a rate that the mixture moderately refluxed. After 2·5 hours of stirring and refluxing the mixture was decomposed with 4·5 ml of 4% NaOH and the formed precipitate was filtered off under suction. The filtrate was dried with K_2CO_3, diethyl ether was evaporated and the remainder was distilled, yielding 2·6 g (83%) of *IIIa* which was pure according to GLC (Chrom-5, Carbowax 20 M, 180°C) and had b.p. 86—87°C/2·0 kPa (15 Torr): Binovic[12] gives b.p. 89—90°C/1·9 kPa (14 Torr). The ^{1}H NMR spectrum (C^2HCl_3, ppm): 0·96 (3 H, t, $J = 7$ Hz) H in the position δ; 1·20—1·75 (8 H, m) H in the positions 3,4,5 and γ; 2·02—2·46 (4 H, m) H in the positions 2 and 6; 2·46—2·74 (2 H, m) H in the position α; 3·33—3·75 (2 H, m) H in the position β and OH.

1-(4-Oxopentanoyl)piperidine (*VIII*)

A solution of 4-oxopentanoyl chloride[13] (26·9 g, 0·20 mol) in 30 ml of diethyl ether was added dropwise during 1 hour under stirring and cooling with an ice bath to the solution of piperidine (34·1 g, 0·40 mol) in 85 ml of diethyl ether. The mixture was stirred for one additional hour at ambient temperature and then filtered. Diethyl ether was removed from the filtrate by evaporation leaving a residue which was distilled yielding 35·7 g (97%) of *VIII* that was uniform according to GLC (Chrom-5, E 301, 240°C) and had b.p. 159—160°C/1·7 kPa (13 Torr) or 110°C/4·0 Pa (0·03 Torr). For $C_{10}H_{17}NO_2$ (183·3) calculated: 65·54% C, 9·35% H, 7·64% N; found: 65·74% C, 9·62% H, 7·58% N. The ^{1}H NMR spectrum (C^2HCl_3, ppm): 1·59 (6 H, m) H in the positions 3,4 and 5; 2·21 (3 H, s) H in the position ε; 2·44—2·87 (4 H, m) H in the positions β and γ; 3·28 to 3·61 (4 H, m) H in the positions 2 and 6. The infrared spectrum (CCl_4, cm^{-1}): 1 648 (s) ν(CO), 1 721 (s) ν(CO), 2 865 (m) ν(CH_2), 2 950 (s) ν(CH_2).

5-(1-Piperidyl)-2-pentanol (*IIIe*)

This compound was prepared by the reduction of *VIII* (31·6 g, 0·17 mol in 80 ml of diethyl ether) with 70% $LiAlH_4$ (8·1 g, 0·15 mol in 750 ml of diethyl ether) in a way as described in the preparation of *IIIa*. Yield 22·5 g (76%) of alcohol *IIIe*, b.p. 115°C/1·7 kPa (13 Torr), pure according to GLC (Chrom-5, Carbowax 20 M, 220°C). D'Ianni and Adkins[14] report b.p. 107°C/0·8 kPa (6 Torr). The ^{1}H NMR spectrum (C^2HCl_3, ppm): 1·16 (3 H, t, $J = 6$ Hz) H in the position ε; 1·26—1·88 (10 H, m) H in the positions 3,4,5, β and γ; 2·12—2·78 (6 H, m) H in the positions 2,6 and α; 3·68 (1 H, m, $J_{\gamma,\delta} = J_{\delta,\varepsilon} = 6$ Hz) H in the position δ; 7·24 (1 H, s) OH.

1-(1-Piperidyl)-3-pentanol (*IIId*)

A solution of 1-(1-piperidyl)-3-pentanone[15] (2·6 g, 0·015 mol) in 6 ml of ether was added dropwise during 20 min under stirring and cooling with bath (−5 to −10°C) to the suspension of 70% $LiAlH_4$ (0·6 g, 0·01 mol) in 80 ml of diethyl ether. The mixture was stirred for additional 30 min under cooling, then 1 hour at the ambient temperature and then left to stand overnight. The reaction mixture was decomposed with 2·4 ml of 4% NaOH, the precipitate was filtered and the ether solution was dried with K_2CO_3. Solvents were removed by column distillation and the residue was distilled yielding 2·0 g (76%) of alcohol *IIId* which was pure according to GLC (Chrom-5, Carbowax 20 M, 200°C) and had b.p. 106—108°C/2·0 kPa (15 Torr); Hromatka[16] gives b.p. 110°C/2·0 kPa (15 Torr). The ^1H NMR spectrum (C^2HCl_3, ppm): 0·93 (3 H, t, $J =$ $= 6$ Hz) H in the position ε; 1·29—1·77 (10 H, m) H in the positions 3,4,5, β and δ; 2·14—2·43 (2 H, m) H in the position α; 2·43—2·79 (4 H, m) H in the positions 2 and 6; 3·50—3·79 (1 H, m) H in the position γ; 6·47 (1 H, s) OH. The infrared spectrum (CCl_4, cm^{-1}): 3 250 ν(OH).

Elemental analyses were performed in the Analytical Laboratory of our Department (head Dr L. Helešic). The NMR *spectra were measured under the direction of Dr P. Trška, the mass spectra were recorded by Dr P. Zachař, the* IR *spectra were measured by Dr E. Janečková and Dr A. Kohoutová.*

REFERENCES

1. Ferles M., Kafka S.: This Journal *47*, 2150 (1982).
2. Ferles M., Kafka S.: This Journal *48*, 1068 (1983).
3. Kono H., Hooz J.: Org. Syn. *53*, 77 (1973).
4. Ferles M., Polívka Z.: This Journal *33*, 2121 (1968).
5. Linstead R. P., Rydon H. N.: J. Chem. Soc. *1934*, 1995.
6. Allan L. T., Swan G. A.: J. Chem. Soc. *1965*, 5704.
7. U.S. Borax Corporation: Brit. 952 811 (1964); Chem. Abstr. *61*, 2970 (1964).
8. Vejdělek Z., Trčka V.: This Journal *24*, 1860 (1959).
9. La Forge F. B., Green N., Gersdorff W. A.: J. Amer. Chem. Soc. *70*, 3707 (1948).
10. Glacet Ch.: Bull. Soc. Chim. Fr. *1954*, 575.
11. Solovyev V. M.: Zh. Obshch. Khim. *31*, 2577 (1961).
12. Binovic K.: Bull. Soc. Chim. Fr. *1957*, 167.
13. Rips R., Derappe Ch., Buu-Hoi N. P.: J. Org. Chem. *25*, 390 (1960).
14. D'Ianni J. D., Adkins H.: J. Amer. Chem. Soc. *61*, 1675 (1939).
15. Brown E., Ragault M., Touet J.: Bull. Soc. Chim. Fr. *1971*, 2195.
16. Hromatka O.: Ber. Deut. Chem. Ges. *75*, 379 (1942).

Translated by S. Heřmánek.