HYDROBORATION OF N-ALLYL DERIVATIVES OF PYRROLIDINE, PIPERIDINE, HEXAHYDROAZEPINE AND MORPHOLINE*

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Heating of allyl derivatives *I* with triethylamine-borane gave spirocyclical amine-boranes *II*, which were hydrolysed with hydrochloric acid to hydrochlorides of aminoboronic acids, *III*. Oxidation of these hydrochlorides produced amino alcohols *IV*.

The preceding papers of this series describe hydroboration of 1-methyl-3-piperideine[1] and other similar unsaturated amines having an allyl type double bond[2-5]. We were interested to know how N-allyl derivatives of some saturated nitrogen heterocycles would behave in the hydroboration. For this purpose N-allyl derivatives of pyrrolidine, piperidine, hexahydroazepine and morpholine were exposed to the action of triethylamine-borane at elevated temperatures. The reaction gave good yields of liquid products, whose analytical and spectral data identified them as spirocyclical amine-boranes *II*.

The infrared spectra of boranes *IIa–IId* contain absorption bands associated with the stretching vibrations of C–H bonds (in the region 2 850–3 010 cm^{-1}) and the the B–H bonds (2 210–2 400 cm^{-1}), deformation vibrations of the C–H bonds (1 435–1 475 cm^{-1}) and deformation vibrations of the B–H bonds (close to the wave number 1 190 cm^{-1} and in the region 1 120–1 131 cm^{-1}). The spectra lack the absorption bands of the BH bridges (the region 1 970–2 180 cm^{-1}), which were found in the spectra of 1,1-dimethyl-1-aza-2-boracycloalkanes[6].

The B–N bond in the molecules of *IIa–IId* manifests itself in the ^1H NMR spectra, ^{11}B NMR spectra and mass spectra as follows: *1*) In the ^1H NMR spectra the signals of the methylene groups bound to nitrogen are shifted to higher values of ppm compared to the corresponding amino alcohols *IVa–IVd*. This demonstrates that the electron density on the nitrogen atom is diminished by the influence of a neighbouring group, strongly attracting electrons (here the BH_2 group only). *2*) The ^{11}B NMR spectra show triplets corresponding to a boron atom split by two atoms of hydrogen. The values of chemical shift, −25·1 to −22·5 ppm (trimethyl borate

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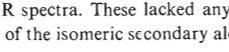
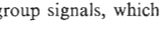
as standard), show that the boron atom occurs in the hybridization sp^3 (refs[7,8]). The *p*-orbital can be made up only by π electrons from the nitrogen atom. *3*) In the mass spectra molecular ions have low intensity, whereas ions $(M-1)^+$ are very intense. An ion $(M-1)^+$ is produced from a molecule with a dative bond between nitrogen and boron by releasing one hydrogen atom bound to a boron atom, followed by formation of a covalent bond between the nitrogen and the boron atoms $\left(-\overset{|}{\underset{|}{\overset{+}{N}}}-BH-\right)$; refs[9,10].

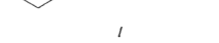
The amine-boranes *II* were hydrolysed with hydrochloric acid in acetone at elevated temperatures to hydrochlorides of aminoboronic acids *III*. These were oxidized with hydrogen peroxide in the presence of sodium hydroxide to pure, primary amino alcohols *IV*. Their structure was corroborated, among other evidence, by ^{1}H NMR spectra. These lacked any methyl group signals, which would suggest admixtures of the isomeric secondary alcohols.



I



II



III

IV

In formulae *I*–*IV*: *a*, X = $(CH_2)_2$; *b*, X = $(CH_2)_3$; *c*, X = $(CH_2)_4$; *d*, = CH_2—O—CH_2.

EXPERIMENTAL

The temperature data are not corrected. The infrared spectra were measured with a spectrophotometer Perkin–Elmer, Model 325. The ^{1}H NMR spectra were measured at 37°C with an apparatus Varian XL-100-15 (100·1 MHz), or Tesla BS-567 (100·1 MHz). The internal standards were tetramethylsilane for samples dissolved in an organic solvent, and sodium 4,4-dimethyl-4-silapentane-1-sulphonate for samples dissolved in deuterium oxide. The ^{11}B NMR spectra were measured at 37°C with an apparatus Varian XL-100-15 (32·1 MHz), trimethyl borate being used as standard. The chemical shifts are designated as negative if the signals occur in a higher magnetic field than would correspond to the resonance of the standard. The mass spectra were measured with an apparatus Gas Chromatograph-Mass Spectrometer LKB 9000 Produkter AB Stockholm. The ionic species are given in units *m*/*z* (% of relative intensity).

5-Aza-1-boraspiro[4,4]nonane (*IIa*)

A mixture of 1-allylpyrrolidine[11] (*Ia*, 17·8 g, 0·16 mol) and triethylamine-borane[12] (18·4 g, 0·16 mol) under nitrogen and a reflux condenser was heated in a bath (150°C) until it started

boiling, then allowed to cool down. The reflux condenser was replaced by a Liebig condenser and triethylamine was distilled off under nitrogen, the bath temperature being heated up to 200°C. The residue was distilled twice over a column *in vacuo*, while nitrogen was introduced through a capillary. Yield 8·5 g (42·5%) of a product boiling at 106–110°C/1·6 kPa (12 Torr). For $C_7H_{16}BN$ (125·0) calculated: 67·24% C, 12·90% H, 8·65% B, 11·20% N; found: 67·21% C, 12·97% H, 9·10% B, 11·21% N. ^{1}H NMR spectrum ($CDCl_3$), ppm: 0·57–1·03 (2 H, m) B–CH_2; 1·59–2·32 (6 H, m) H in positions 3, 7 and 8; 2·53–2·97 (4 H, m) and 3·05–3·50 (2 H, m) H in positions 4, 6 and 9. ^{11}B NMR spectrum (octadeuteriodioxan), ppm: −23·4 (1 B, t, J = 100 Hz). Mass spectrum: 124 (100), 123 (29), 84 (59), 82 (69), 54 (30), 40 (32). IR spectrum (CCl_4), cm^{-1}: 878 (m), 908 (m), 950 (m), 1 033 (m), 1 085 (m), 1 106 (i), 1 131 (s) δ(BH), 1 193 (s) δ(BH), 1 303 (m), 1 310 (m), 1 350 (m), 1 370 (w), 1 435 (i) δ(CH_2), 1 451 (i) δ(CH_2), 1 460 (s) δ(CH_2), 1 475 (i) δ(CH_2), 2 210 (m) ν(BH_2), 2 300 (s) ν(BH_2), 2 360 (i) ν(BH_2), 2 390 (s) ν(BH_2), 2 850 (s) ν(CH_2), 2 880 (s) ν(CH_2), 2 910 (i) ν(CH_2), 2 940 (s) ν(CH_2), 2 960 (i) ν(CH_2), 2 990 (i) ν(CH_2).

5-Aza-1-boraspiro[4,5]decane (*IIb*)

This was prepared analogously to *IIa* from 1-allylpiperidine[13] (*Ib*, 62·6 g, 0·50 mol) and triethylamine-borane[12] (57·5 g, 0·50 mol). The reaction, which occurred at a bath temperature of 145°C, manifested itself by a vigorous boil and continued for a few minutes after the bath had been removed; yield 28·0 g (40%), b.p. 125°C/1·7 kPa (13 Torr). For $C_8H_{18}BN$ (139·1) calculated: 69·10% C, 13·05% H, 7·78% B, 10·07% N; found: 69·22% C, 13·29% H, 7·68% B, 10·24% N. ^{1}H NMR spectrum (Tesla, $CDCl_3$), ppm: 0·45–1·00 (2 H, m) B–CH_2; 1·20–2·25 (8 H, m) H in positions 3, 7, 8 and 9; 2·40–3·16 (6 H, m) H in positions 4, 6 and 10. ^{11}B NMR spectrum ($CDCl_3$), ppm: −25·1 (1 B, t, J = 100 Hz). Mass spectrum: 138 (100), 137 (29), 98 (56), 96 (42), 86 (28), 84 (42), 54 (29). IR spectrum ($CHCl_3$), cm^{-1}: 864 (w), 894 (w), 910 (s), 960 (w), 978 (w), 1 015 (w), 1 030 (i), 1 040 (m), 1 078 (w), 1 088 (w), 1 120 (s) δ(BH_2), 1 190 (m) δ(BH_2), 1 290 (m), 1 323 (m), 1 346 (m), 1 375 (m), 1 396 (w), 1 417 (w), 1 438 (m) δ(CH_2), 1 448 (m), δ(CH_2), 1 456 (s) δ(CH_2), 1 465 (i) δ(CH_2), 1 474 (m) δ(CH_2), 2 220 (m) ν(BH_2), 2 300 (s) ν(BH_2), 2 340 (i) ν(BH_2), 2 370 (i) ν(BH_2), 2 400 (i) ν(BH_2), 2 870 (s) ν(CH_2), 2 940 (s) ν(CH_2), 3 010 (s) ν(CH_2).

5-Aza-1-boraspiro[4,6]undecane (*IIc*)

The amine-borane *IIc* was prepared from 1-allylhexahydroazepine[14] (*Ic*, 7·0 g, 0·05 mol) and triethylamine-borane[12] (5·8 g, 0·05 mol) as described for *IIa*; yield 2·6 g (34%), b.p. 126–128°C/1·7 kPa (13 Torr). For $C_9H_{20}BN$ (153·1) calculated: 70·61% C, 13·17% H, 7·07% B, 9·15% N; found: 70·43% C, 13·14% H, 6·95% B, 9·16% N. ^{1}H NMR spectrum (Tesla, $CDCl_3$), ppm: 0·49–0·98 (2 H, m) B–CH_2; 1·40–2·15 (10 H, m) H in positions 3, 7, 8, 9 and 10; 2·60–3·35 (6 H, m) H in positions 4, 6 and 11. ^{11}B NMR spectrum ($CDCl_3$), ppm: −22·5 (1 B, t, J = 100 Hz). Mass spectrum: 152 (100), 151 (29), 150 (20), 112 (55), 110 (19), 82 (42), 54 (23). IR spectrum ($CHCl_3$), cm^{-1}: 830 (w), 862 (m), 911 (w), 975 (w), 1 000 (m), 1 012 (w), 1 033 (m), 1 053 (m), 1 095 (m), 1 105 (i), 1 130 (s) δ(BH_2), 1 190 (m), δ(BH_2), 1 294 (w), 1 315 (w), 1 346 (w), 1 365 (w), 1 440 (m) δ(CH_3), 1 453 (m) δ(CH_2), 1 470 (s) δ(CH_2), 2 230 (m) ν(BH_2), 2 300 (s) ν(BH_2), 2 340 (i) ν(BH_2), 2 370 (i) ν(BH_2), 2 860 (s) ν(CH_2), 2 940 (s) ν(CH_2), 2 990 (i) ν(CH_2).

5-Aza-1-bora-8-oxaspiro[4,5]decane (*IId*)

Adhering to the procedure for the synthesis of *IIa*, the amine-borane *IId* was prepared from 4-allylmorpholine[15] (*Id*, 63·6 g, 0·50 mol) and triethylamine-borane[12] (57·5 g, 0·50 mol). The reaction started at a bath temperature of 140°C and manifested itself by a vigorous boil, which

persisted several minutes after the bath had been removed; yield 28·5 g (40%), b.p. 128·5°C/1·8 kPa (13·5 Torr). For $C_7H_{16}BNO$ (141·0) calculated: 59·62% C, 11·44% H, 7·67% B, 9·93% N; found: 59·74% C, 11·57% H, 8·02% B, 10·11% N. ^{1}H NMR spectrum (octadeuteriodioxan), ppm: 0·62 (2 H, q, J = 7 Hz) B—CH_2; 1·21 (2 H, q, J = 7 Hz) B—C—CH_2; 2·20–3·10 (6 H, m) H in positions 4, 6, and 10; 3·47–4·15 (4 H, m) H in positions 7 and 9. ^{11}B NMR spectrum (octadeuteriodioxan), ppm: −25·1 (1 B, t, J = 100 Hz). Mass spectrum: 140 (100), 139 (26), 112 (34), 100 (67), 98 (53); 84 (44), 70 (69), 56 (38), 54 (51), 42 (53), 40 (40). IR spectrum (CCl_4), cm^{-1}: 872 (m), 900 (w), 922 (m), 935 (m), 955 (w), 990 (m), 1 023 (m), 1 064 (m), 1 080 (m), 1 120 (s) $\delta(BH_2)$, 1 165 (w), 1 192 (m) $\delta(BH_2)$, 1 240 (w), 1 277 (m), 1 302 (m), 1 316 (m), 1 334 (w), 1 349 (m), 1 446 (m) $\delta(CH_2)$, 1 457 (m) $\delta(CH_2)$, 1 466 (m) $\delta(CH_2)$, 2 340 (s) $\nu(BH_2)$, 2 400 (s) $\nu(BH_2)$, 2 850 (i) $\nu(CH_2)$, 2 880 (s) $\nu(CH_2)$, 2 910 (i) $\nu(CH_2)$, 2 940 (s) $\nu(CH_2)$, 2 970 (s) $\nu(CH_2)$.

Hydrochloride of 3-Pyrrolidinopropylboronic Acid (*IIIa*)

To a solution of *IIa* (5·5 g, 0·044 mol) in acetone (44 ml) was added dropwise 15% hydrochloric acid (26·5 ml) under stirring, while the mixture spontaneously heated up and hydrogen evolved. The mixture was then stirred and boiled for 15 min, then taken to dryness. A portion (3·2 g, 38%) of the residue (8·5 g) was repeatedly crystallized from 2-propanol; yield 1·3 g (41%) of *IIIa*, m.p. 132–134°C. For $C_7H_{17}BClNO_2$ (193·50) calculated: 43·45% C, 8·86% H, 5·59% B, 18·32% Cl, 7·24% N; found: 43·64% C, 9·03% H, 5·64% B, 18·31% Cl, 7·44% N. ^{1}H NMR spectrum (D_2O), ppm: 0·78 (2 H, t, J = 8 Hz) CH_2—B; 1·56–2·28 (6 H, m) CH_2—C—B and H in positions 3 and 4 of the pyrrolidine ring; 3·02–3·66 (6 H, m) H of the methylene groups bound to the nitrogen atom. IR spectrum (KBr pellet), cm^{-1}: 735 (s), 766 (s), 803 (s), 868 (w), 908 (w), 955 (w), 1 003 (m), 1 022 (m), 1 045 (m), 1 070 (s), 1 106 (s), 1 155 (w), 1 180 (m), 1 213 (m), 1 265 (s), 1 308 (s), 1 340 (s), 1 355 (s), 1 395 (s), 1 442 (s), 2 110 (w), 2 260 (w), 2 350 (w), 2 490 (s), 2 590(s), 2 620 (s), 2 680 (s), 2 880 (s), 2 960 (s), 3 240 (s), 3 370 (s).

Hydrochloride of 3-Piperidinopropylboronic Acid (*IIIb*)

Like in the preparation of *IIIa*, a solution of *IIb* (13·9 g, 0·10 mol) in acetone (100 ml) was hydrolysed with 15% hydrochloric acid (60 ml). A portion (10·0 g, 45%) of the crude product (22·1 g) was repeatedly crystallized; yield 5·9 g (63%) of *IIIb*, m.p. 217–220°C (2-propanol). For C_8H_{19}.$BClNO_2$ (207·5) calculated: 46·30% C, 9·23% H, 5·21% B, 17·09% Cl, 6·75% N; found: 46·23% C, 9·48% H, 5·08% B, 17·01% Cl, 6·74% N. ^{1}H NMR spectrum (Tesla, D_2O), ppm: 0·80 (2 H, t, J = 8 Hz) CH_2—B; 1·26–2·20 (8 H, m) CH_2—C—B and H in positions 3, 4 and 5 of the piperidine ring; 2·70–3·12 (4 H, m) and 3·18–3·46 (2 H, m) H of the methylene groups bound to the nitrogen atom. IR spectrum (KBr pellet), cm^{-1}: 496 (w), 583 (w), 630 (m), 734 (m), 765 (m), 805 (m), 825 (m), 860 (w), 902 (w), 980 (s), 1 000(s), 1 015 (m), 1 033 (w), 1 068 (s), 1 105 (s), 1 137 (m), 1 190 (w), 1 220 (m), 1 258 (w), 1 282 (m), 1 306 (m), 1 323 (s), 1 340 (m), 1 349 (s), 1 362 (s), 1 376 (s), 1 390 (s), 1 399 (s), 1 439 (s), 1 455 (s), 1 467 (s), 1 625 (w), 2 560 (s), 2 590 (m), 2 670 (s), 2 720 (m), 2 750 (m), 2 890 (m), 2 950 (s), 3 240 (s), 3 370 (s).

Hydrochloride of 3-(1-Hexahydroazepinyl)propylboronic Acid (*IIIc*)

In analogy to the preparation of *IIIa*, *IIIc* was obtained by hydrolysis of *IIc* (3·9 g, 0·026 mol) with 15% hydrochloric acid (15·5 ml) in acetone (25·5 ml); yield 2·0 g (36%), m.p. 139–144°C (2-propanol). For $C_9H_{21}BClNO_2$ (221·6) calculated: 48·79% C, 9·55% H, 4·88% B, 16·00% Cl, 6·32% N; found: 48·83% C, 9·66% H, 4·91% B, 16·29% Cl, 6·49% N. ^{1}H NMR spectrum (Tesla,

D_2O), ppm: 0·80 (2 H, t, $J = 8$ Hz) CH_2—B; 1·46—2·06 (10 H, m) CH_2—C—B and H in positions 3, 4, 5 and 6 of the hexahydroazepine ring; 2·78—3·65 (6 H, m) H of the methylene groups bound to the nitrogen atom. IR spectrum (KBr pellet), cm^{-1}: 492 (w), 565 (w), 630 (w), 735 (m), 800 (m), 843 (w), 880 (w), 913 (w), 980 (m), 1 013 (m), 1 055 (m), 1 080 (m), 1 103 (m), 1 153 (w), 1 215 (w), 1 275 (w), 1 310 (m), 1 324 (m), 1 349(s), 1 362 (m), 1 375 (m), 1 384 (m), 1 400 (m), 1 431 (m), 1 440 (m), 1 470 (m), 1 625 (w), 2 540 (w), 2 580 (w), 2 650 (m), 2 680 (m), 2 720 (m), 2 860 (m), 2 935 (s), 3 270 (s), 3 380 (s).

Hydrochloride of 3-Morpholinopropylboronic Acid (*IIId*)

This was prepared, in analogy to *IIIa*, by hydrolysis of *IId* (2·8 g, 0·02 mol) with 15% hydrochloric acid (12 ml) in acetone (20 ml); yield 3·4 g (82%), m.p. 148—151°C (2-propanol). For C_7H_{17}. .$BClNO_3$ (209·5) calculated: 40·13% C, 8·18% H, 5·16% B, 16·92% Cl, 6·69% N; found: 40·24% C, 8·22% H, 5·45% B, 17·18% Cl, 6·70% N. ^{1}H NMR spectrum (D_2O), ppm: 0·82 (2 H, t, $J = 7$ Hz) CH_2—B; 1·57—2·10 (2 H, m) CH_2—C—B; 3·00—3·46 (6 H, m) H of the methylene groups bound to the nitrogen atom, 3·95 (4 H, m) CH_2—OCH_2. IR spectrum (KBr pellet), cm^{-1}: 620 (w), 736 (m), 760 (w), 778 (w), 805 (m), 836 (w), 845 (w), 877 (s), 910 (m), 973 (m), 1 006 (m), 1 015 (m), 1 038 (m), 1 066 (s), 1 081 (s), 1 117 (s), 1 133 (m), 1 200 (w), 1 212 (w), 1 260 (m), 1 270 (m), 1 300 (m), 1 309 (m), 1 323 (s), 1 337 (s), 1 351 (s), 1 378 (s), 1 404 (s), 1 442 (s), 1 460 (m), 1 480 (m), 1 640 (w), 1 990 (w), 2 100 (w), 2 260 (w), 2 340 (w), 2 490 (m), 2 520 (m), 2 570 (s), 2 600 (s), 2 630 (s), 2 660 (s), 2 690 (s), 2 725 (m), 2 760 (m), 2 790 (m), 2 880 (s), 2 950 (s), 2 970 (s), 3 260 (s), 3 380 (s).

3-Pyrrolidino-1-propanol (*IVa*)

The remaining 5·2 g (62%) of the residue of the reaction mixture after hydrolysis of *IIa* was stirred up in tetrahydrofuran (45 ml); 40% sodium hydroxide (27 ml) was added, then 30% hydrogen peroxide (45 ml) was added dropwise under stirring. The addition of the peroxide raised the temperature of the mixture to the boiling point. The mixture was then stirred and boiled for 3 h. After cooling the organic layer was separated and the aqueous layer was extracted with five 30 ml portions of ether. The extract and the organic layer were combined and dried with potassium carbonate. The desiccant was removed by filtration and the ether was distilled off over a column; yield of *IVa* 2·0 g (58%), b.p. 92°C/1·6 kPa (12 Torr). The reported[16] b.p. 92 to 95°C/1·5 kPa (11 Torr). ^{1}H NMR spectrum ($CDCl_3$), ppm: 1·70—2·00 (6 H, m) CH_2—C—O and H in positions 3 and 4 of the pyrrolidine ring; 2·40—2·84 (6 H, m) H of the methylene groups bound to the nitrogen atom; 3·72 (2 H, t, $J = 5{\cdot}5$ Hz) CH_2—O; 5·20 (1 H, s) OH. IR spectrum ($CHCl_3$), cm^{-1}: 1 075 (s), δ(OH), 3 040—3 600 ν(OH).

3-Piperidino-1-propanol (*IVb*)

11·9 g of the crude *IIIb* gave 5·9 g (81%) of *IVb*, b.p. 100°C/1·6 kPa (12 Torr). For the procedure see the preparation of *IVa* (90 ml of tetrahydrofuran, 54 ml of 40% sodium hydroxide, 90 ml of 30% hydrogen peroxide). Reported[17] b.p. 93·5—95°C/1·5 kPa (11 Torr). ^{1}H NMR spectrum (Tesla, $CDCl_3$), ppm: 1·25—1·88 (8 H, m) CH_2—C—O and H in positions 3, 4 and 5 of the piperidine ring; 2·28—2·70 (6 H, m) H of the methylene groups bound to the nitrogen atom; 3·78 (2 H, t, $J = 5$ Hz) CH_2—O; 5·62 (1 H, s) OH. IR spectrum ($CHCl_3$), cm^{-1}: 3 000—3 560 ν(OH).

3-(1-Hexahydroazepinyl)propanol (*IVc*)

This compound was prepared, in analogy to *IVa*, by hydrolysis of *Ic* (1·8 g, 0·012 mol) with 15% hydrochloric acid (7·5 ml) in acetone (12 ml), followed by oxidation of the hydrolytic product with 30% hydrogen peroxide (20·5 ml) in a mixture of tetrahydrofuran (20·5 ml) and 40% sodium hydroxide (12 ml). Yield 1·4 g (76%), b.p. 110°C/1·6 kPa (12 Torr); ref.[18] b.p. 115–117°C/1·6 kPa (12 Torr). ^{1}H NMR spectrum ($CDCl_3$), ppm: 1·42–2·00 (10 H, m) CH_2—C—O and H in positions 3, 4, 5 and 6 of the hexahydroazepine ring, 2·50–2·90 (6 H, m) H of the methylene groups bound to the nitrogen atom, 3·80 (2 H, t, J = 5 Hz) CH_2—O, 5·77 (1 H, s) OH. IR spectrum ($CHCl_3$), cm^{-1}: 1 067 (s) δ(OH), 3 000–3 580 ν(OH).

3-Morpholinopropanol (*IVd*)

This was obtained, analogously to *IVa*, by hydrolysis of *IIa* (2·9 g, 0·021 mol) with 15% hydrochloric acid (12·5 ml) in acetone (21 ml), followed by oxidation of the hydrolytic product with 30% hydrogen peroxide (35·5 ml) in a mixture of tetrahydrofuran (35·5 ml) and 40% sodium hydroxide (21 ml). Yield 2·1 g (70%), b.p. 109–113°C/1·5 kPa (11 Torr). The literature gives b.p. 134–136°C/24 Torr (ref.[19]), 143–145°C/3·7 kPa (28 Torr) (ref.[20]) and 95°C/0·1 kPa (1 Torr) (ref.[21]). ^{1}H NMR spectrum ($CDCl_3$), ppm: 1·73 (2 H, q, J = 6 Hz) C—CH_2—C, 2·44–2·70 (6 H, m) H of the methylene groups bound to the nitrogen atom, 3·64–3·88 (6 H, m) H of the methylene groups bound to the oxygen atoms, 4·85 (1 H, s) OH. Mass spectrum: 145 (8·5), 100 (100). IR spectrum ($CHCl_3$), cm^{-1}: 3 000–3 560 ν(OH).

The elemental analyses were performed at the Analytical Laboratory of our Department (head Dr L. Helešic). The NMR *spectra were measured under the direction of Dr P. Trška, mass spectra were measured by Dr J. Mitera and Dr J. Novák,* IR *spectra by Dr E. Janečková and Dr A. Kohoutová.*

REFERENCES

1. Polívka Z., Ferles M.: This Journal *35*, 2392 (1970).
2. Ferles M., Hauer J., Kolář J., Polívka Z., Štern P.: This Journal *37*, 2464 (1972).
3. Ferles M., Štern P., Trška P., Vyšata F.: This Journal *38*, 1206 (1973).
4. Štern P., Trška P., Ferles M.: This Journal *39*, 2267 (1974).
5. Ferles M., Štern P., Trška P.: This Journal *39*, 3317 (1974).
6. Polívka Z.: *Thesis*, p. 25. Prague Institute of Chemical Technology, Prague 1969.
7. Nagasawa K., Yoshizaki T., Watanabe H.: Inorg. Chem. *4*, 275 (1965).
8. Philips W. D., Miller H. C., Muetterties E. L.: J. Amer. Chem. Soc. *81*, 4496 (1959).
9. Polívka Z., Ferles M.: This Journal *34*, 3009 (1969).
10. Polívka Z., Kubelka V., Holubová N., Ferles M.: This Journal *35*, 1131 (1970).
11. Lukevics E. Ya., Moskovich R. Ya., Satc V. D.: Izv. Akad. Nauk Latv. SSR, Ser. Khim. *1976*, 53; Ref. Zh. Khim. *1976*, 16Zh398.
12. U.S. Borax Corporation: Brit. 952,811 (1964); Chem. Abstr. *61*, 2970 (*1964*).
13. Cromwell N. H., Hassner A.: J. Amer. Chem. Soc. *77*, 1568 (1955).
14. Čermák J.: *Thesis*. Prague Institute of Chemical Technology, Prague 1981.
15. Butler G. B., Bunch R. L.: J. Amer. Chem. Soc. *71*, 3120 (1949).
16. Mikhlina E. E., Vorob'eva V. Ya., Bobyleva S. S., Medvedev B. A., Rubtsov M. V.: Khim.-Farm. Zh. *1* (8), 35 (1967).

17. Clinton R. O.: U.S. 2, 608, 574 (1952); Chem. Abstr. *47*, 5964 (1953).
18. Blicke F. F., Doorenbos N. J.: J. Amer. Chem. Soc. *76*, 2317 (1954).
19. Gardner J. H., Haenni E. O.: J. Amer. Chem. Soc. *53*, 2763 (1931).
20. Hromatka O.: Ber. Deut. Chem. Ges. *75B*, 131 (1942).
21. Hannig E., Bekemeier H.: Pharmazie *14*, 201 (1959); Chem. Abstr. *54*, 278 (1960).

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