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Journal of Organometallic Chemistry 534 (1997) 181–186

Journal of Organometallic Chemistry

Synthesis of bicyclic N-pyrrolylboranes via hydroboration of 2-vinyl and 2-allylpyrrole

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Received 10 October 1996

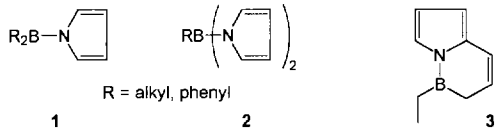
Abstract

The hydroboration of 2-vinyl and 2-allylpyrrole with various hydroborating agents [$Et_2BH_2BEt_2$, $(9\text{-BBN})_2$, $(CH_2)_4BH_2B(CH_2)_4$, thex(H)BH_2B(H)thex, Az-BH_2–THF (Az = pyrrole, 2,5-dimethylpyrrole, indole), Et_2O–BH_2Cl, $Me_3Si(H)NB_2H_5$] leads in most cases finally to B-substituted bicyclic N-pyrrolylboranes **8–11**, **15–20**. In the case of the reaction with tetraalkyldiboranes(6), stable intramolecular 2-H-pyrrole-borane adducts **6**, **7**, **12–14** are formed first which, in the case of **6**, **12** and **13**, can be converted into the bicyclic N-pyrrolylboranes **8**, **15** and **16** respectively. Although the steric conditions in the bicyclic N-pyrrolylboranes are favourable, ^{11}B, ^{13}C and ^{14}N NMR data do not support any significant π interactions between the boron atoms and the heteroaromatic pyrrole system.

Keywords: Boron; Pyrrole; Hydroboration; NMR

1. Introduction

The synthesis of organoboranes such as **1** or **2** with one or two N-pyrrolyl groups attached to the boron atom has been reported [1–3]. The bonding situation in these compounds is of interest since they are related to aminoboranes where the BN bond has double bond character, and they can also be compared with arylboranes considering that the heteroaromatic pyrrole system requires the lone pair of electrons at the nitrogen atom. The molecular structures of tri-N-pyrrolylborane and tri-N-(2,5-dimethylpyrrolyl)borane do not provide convincing evidence for BN(pp)π interactions [4]. In order to increase the probability for BN(pp)π interactions, bicyclic N-pyrrolylboranes should be suitable candidates. Recently we have shown that pyrrole derivatives such as **3** become available either directly or indirectly from N,C-dilithio-2-allylpyrrole [5]. Another convenient access to bicyclic N-pyrrolylboranes should take advantage of the presumably stereoselective hydroboration [6] of 2-vinyl (**4**) or 2-allylpyrrole (**5**). Therefore we have studied the reactivity of **4** and **5** towards various hydroborating agents such as tetraalkyldiboranes(6), 1,2-dithexyldiborane(6) in THF [6], N-azolylboranes in THF [7], chloroborane in ether [6], and N-trimethylsilyl-μ-aminodiborane(6) [8].



1 2 3

2. Results and discussion

2.1. Hydroboration of 2-vinylpyrrole

As shown in Scheme 1, the reactions of 2-vinylpyrrole **4** with tetraalkyldiboranes(6) in THF proceeded smoothly to give immediately the intramolecular adducts **6** and **7** as a result of stereoselective hydroboration and a 1,2-hydrogen shift from nitrogen to the adjacent carbon atom. Heating of **6** at 80 °C afforded the desired bicyclic N-pyrrolylborane **8** by liberation of ethane. In the case of the adduct **7**, heating above 160 °C led only to decomposition. If 1,2-dithexyldiborane or N-azolylboranes in THF were used, the formation of the adducts corresponding to **6** or **7**, as most likely interme-

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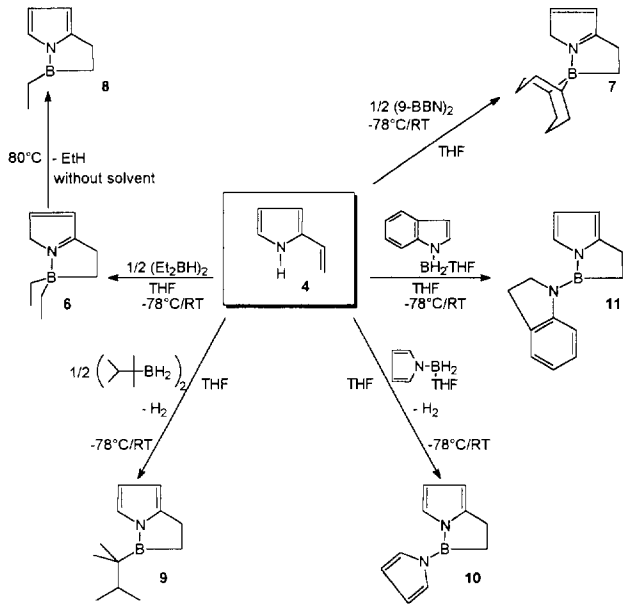
PII S0022-328X(96)06921-5



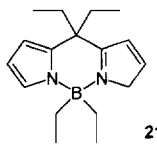
Scheme 1.

diates, was not observed. Instead, the bicyclic N-pyrrolylboranes **9** and **10** were formed as the result of hydroboration followed or accompanied by H_2 elimination. In the case of the reaction of **4** with indolylborane in THF, H_2 elimination was not observed but in the product **11** the boron atom bears an N-2,3-dihydroindolyl group. This means that the H_2 molecule was trapped by the reactive C(2)C(3) double bond of the indolyl group.

2.2. Hydroboration of 2-allylpyrrole

The reactions of 2-allylpyrrole **5** with various hydroborating agents are shown in Scheme 2. The results are closely analogous to those found for 2-vinylpyrrole. However, some types of compounds were accessible which are probably more stable if the boron atom is part of a six-membered ring. The intramolecular adducts **12**, **13** and **14** were obtained from the reaction of **5** with the tetraalkyldiboranes(6). Again it proved possible to convert **12** into **15** just by heating at 100 °C. Somewhat more severe conditions were necessary (130 °C) to obtain **15** by opening the boratacyclopentane ring in **13**. Heating of **14** at 160 °C gave only unidentified decomposition products. 1,2-Dithexyldiborane(6) and N-pyrrolylborane in THF reacted with **5** by H_2 elimination to give **17** and **18** respectively again, as found for **9** and **10** (Scheme 1), without a detectable intermediate. Interestingly, the use of Et_2O–BH_2Cl afforded **19** by an analogous course of the reaction. The bicyclic N-pyrrolylborane **19** is the first example of an N-pyrrolylborane with a B–halogen bond. Previous attempts at the synthesis of such compounds led only to unidentified polymeric material. Another derivative **20** with a functional group at the boron atom was isolated from the complex reaction mixture when **5** reacted with N-trimethylsilyl-μ-aminodiborane(6).

Intramolecular adducts of the type **6**, **7** (Scheme 1) and **12–14** (Scheme 2) have not been described previously. There is one compound **21**, the product of the reaction of **1** (R = Et) with diethylketone [9], in which this structural fragment is present. However, the apparently straightforward formation of the adducts **6**, **7**, **12–14** suggests that a 2H-pyrrole-borane adduct must be considered as an intermediate in the reaction of pyrrole with BH_3 in THF, which leads first to N-pyrrolylborane-THF [7] and finally to tri-N-pyrrolylborane.



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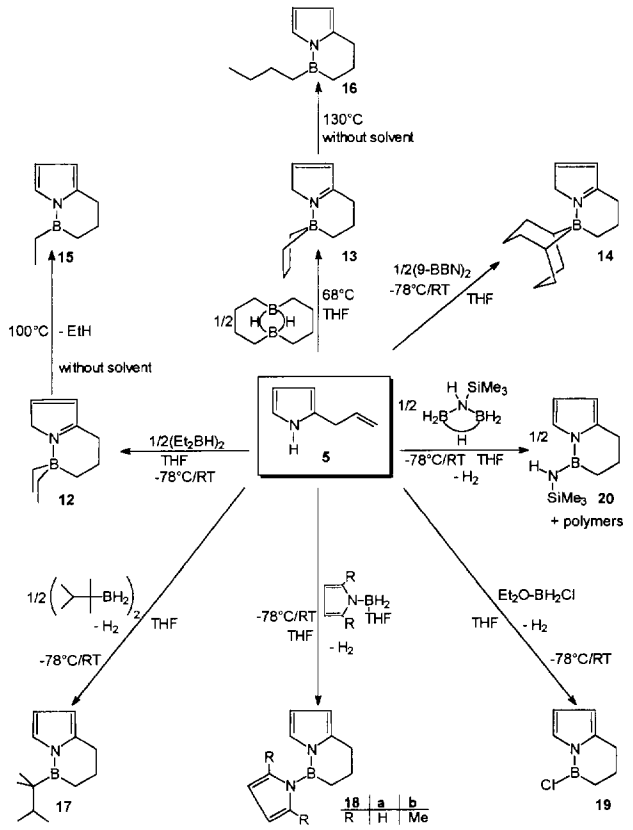
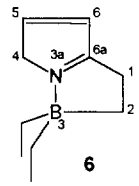
2.3. NMR spectroscopic results

The ^{11}B and ^{13}C NMR data of the adducts **6**, **7** and **12–14** are listed in Tables 1 and 2 respectively. Tables 3 and 4 contain ^{11}B and ^{13}C NMR data of the bicyclic

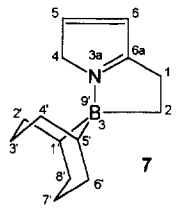


Scheme 2.

Table 1
NMR data[a] of the compounds **6**, **7**



6



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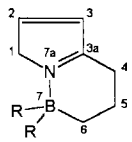
Nr.		**6**	**7**
R		Et	1,5-cyclooctane-diyl
$\delta^{11}B$		1.0	1.5
$\delta^{13}C$	C-1	29.7	29.0
	C-2	18.1 [br]	22.3 [br]
	C-4	58.2	63.2
	C-5	152.5	152.1
	C-6	125.7	125.7
	C-6a	185.9	187.0
	R	17.6 [br] (CH_2)	26.9 [br] (C-1′/5′)
		11.0 (CH_3)	32.5/34.2 (C-2′/4′/6′/8′)
			25.6/25.9 (C-3′/7′)

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.

N-pyrrolylboranes **8**–**11** (Scheme 1) and **15**–**20** (Scheme 2). ^1H NMR data are given in the experimental part.

All NMR data are consistent with the proposed structures. The presence of tetracoordinate boron atoms in the adducts (Tables 1 and 2) is clearly indicated by their $\delta^{11}B$ data [10]. The $\delta^{11}B$ data (Tables 3 and 4) are also typical of the surroundings of the tri-coordinate boron

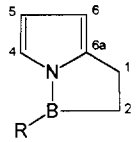
Table 2
^{11}B and ^{13}C NMR data[a] of the compounds **12**–**14**



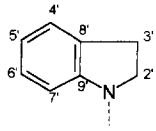
Nr.		**12**[b]	**13**	**14**[c]
R		Et	1,4-butane-diyl	1,5-cyclooctane-diyl[d]
$\delta^{11}B$		−5.1	−3.1	−4.2
$\delta^{13}C$	C-1	62.9	63.0	68.8
	C-2	148.1	147.7	147.5
	C-3	129.8	129.7	129.6
	C-3a	179.1	177.6	179.2
	C-4	30.4	30.3	30.0
	C-5	20.2	20.7	18.0
	C-6	16.8 [br]	22.4 [br]	19.3 [br]
	R	19.5 [br] (CH_2)	27.4 [br] (C-2′/5′)	26.9 [br] (C-1′/5′) 32.5/34.2
		10.9 (CH_3)	30.9 (C-3′/4′)	(C-2′/4′/6′/8′) 25.3/25.5 (C-3′/7′)

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.
[b] $\delta^{14}N = -130.9$.
[c] $\delta^{14}N = -127.7$.
[d] For indication of 1,5-cyclooctane-diyl group see Table 1.

Table 3
^{11}B and ^{13}C NMR data[a] of the compounds **8**–**11**



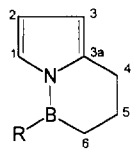
Nr.		**8**	**9**	**10**	**11**
R		Et[b]	thexyl[c]	N-pyrrolyl[d]	N-2,3-dihydroindolyl[e]
$\delta^{11}B$		58.3	59.7	39.3	35.2
$\delta^{13}C$	C-1	22.0	21.6	20.8	22.0
	C-2	17.5 [br]	22.6 [br]	16.6 [br]	17.6 [br]
	C-4	116.9	118.4	116.8	117.2
	C-5	119.3	119.4	119.1	117.4
	C-6	104.5	104.3	104.3	103.5
	C-6a	151.4	152.2	151.5	141.1

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J[^{13}C,^{11}B]$.
[b] $\delta^{13}C$: 9.6 [br] (CH_2); 9.2 (CH_3).
[c] $\delta^{13}C$: 28.8 [br] (B–C); 35.5 (CH); 18.5 (CH_3–C); 21.9 (CH_3–CH).
[d] $\delta^{13}C$: 124.6 (N–*C*H); 113.7.
[e] N-2,3-dihydroindolyl:  $\delta^{13}C$: 49.2 (C-2′); 29.6 (C-3′); 125.0 (C-4′); 127.4 (C-5′); 121.7 (C-6′); 113.4 (C-7′); 127.7 (C-8′); 132.7 (C-9′).

atoms in the bicyclic N-pyrrolylboranes. When compared with $\delta^{11}B$ data of non-cyclic N-pyrrolylboranes of the type **1** or **2** [10], there are only small changes, in contrast to significant effects observed for aminoboranes [10]. This is in agreement with rather weak BN(pp)π bonding in N-pyrrolylboranes. Thus, the similarity between the $\delta^{11}B$ values of aminoboranes and N-pyrrolylboranes is mainly due to the dependence of ^{11}B nuclear shielding in trigonal boranes on σ-bonding effects. The $\delta^{13}C$ values (Tables 3 and 4) provide another sensitive probe for potential (pp)π interactions between the boron atom and the heteroaromatic system. However, the differences between the $\delta^{13}C$ values for the ring carbon atoms are small. If π bonding effects were important, one would expect a much larger range of $\delta^{13}C$ values, depending on the nature of the various substituents R. Even in the case of R = Cl (**19**), where the boron atom should have maximum π acceptor strength, the $\delta^{13}C$ nuclear shielding is hardly affected.

^{14}N chemical shifts ($\delta^{14}N$) are extremely sensitive to π interactions [11]. If one compares the $\delta^{14}N$(pyrrole) values of **15** (−191.2) and **20** (−204), the slightly greater ^{14}N(pyrrole) nuclear shielding in **20** points towards reduced BN(pyrrole)(pp)π interactions in **20**. The ^{14}N(amino) shielding of **20** ($\delta^{14}N = -304$) is only slightly increased as compared to R_2B–N(H)$SiMe_3$ (R = alkyl; $\delta^{14}N = -287$ [12]). Although the changes in the $\delta^{14}N$ values are according to expectations if BN(pyrrole)(pp)π interactions are present, the small magnitude of these effects indicates that such π interac-

Table 4
^{11}B and ^{13}C NMR data[a] of the compounds **15–20**



Nr.		**15**	**16**	**17**	**18a**	**18b**	**19**	**20**
R		Et[b]	^{n}Bu[c]	thexyl[d]	N-pyrrolyl[e]	N-2,5-dimethylpyrrolyl[f]	Cl	N(H)SiMe$_3$[g]
$\delta^{11}B$		55.7	55.6	57.6	37.2	42.3	46.4	35.6
$\delta^{13}C$	C-1	121.0	121.2	123.1	122.2	122.9	121.4	117.1
	C-2	113.3	113.4	113.5	114.1	114.3	114.6	111.9
	C-3	109.8	109.8	109.4	109.7	110.6	110.9	108.2
	C-3a	137.8	137.3	138.5	139.7	138.3	138.3	137.8
	C-4	26.5	26.5	27.2	26.4	26.2	25.6	26.7
	C-5	21.8	21.9	21.9	21.4	22.1	22.1	22.5
	C-6	17.4 [br]	17.0 [br]	19.5 [br]	14.7 [br]	17.0 [br]	18.9 [br]	17.0 [br]

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^1J(^{13}C,^{11}B)$.
[b] $\delta^{13}C$: 12.3 [br] (CH_2); 8.8 (CH_3). $\delta^{14}N = -191.2$.
[c] $\delta^{13}C$: 27.6 (C-2′); 26.3 (C-3′); 14.3 (CH_3); B–CH_2: n.o.
[d] $\delta^{13}C$: 29.9 [br] (B–C); 35.1 (CH); 18.4 (CH_3–C); 22.6 (CH_3–CH). $\delta^{14}N = -192.3$.
[e] $\delta^{13}C$: 124.9 (N–CH); 113.7.
[f] $\delta^{13}C$: 130.7 (N–*C*); 111.0; 14.8 (CH_3).
[g] $\delta^{13}C$: 1.5 $^1J[^{29}Si,^{13}C] = 59.9$ Hz; $\delta^{29}Si$: 6.2 $^1J[^{29}Si,^{15}N] = 14.2$ Hz. $\delta^{14}N = -204$ (pyrrole-N); −304 (Si–N).

tions do not play a significant role, in agreement with the interpretation of ^{11}B and ^{13}C chemical shifts.

3. Conclusions

The formation of bicyclic N-pyrrolylboranes starting from 2-vinyl or 2-allylpyrrole can be achieved by stereoselective hydroboration in the first step, formation of a more or less stable intramolecular adduct with a 2-hydropyrrole fragment in the second step, and elimination of an alkane or H_2 in the final step. Although the stereochemistry of these heterocycles invites BN(pp)π bonding, such interactions appear to be very weak, as follows from a comparison of their NMR data with those for comparable non-cyclic N-pyrrolylboranes.

4. Experimental details

All preparative work and handling of samples was carried out under an atmosphere of dry N_2, using oven-dried glassware and dry solvents. Starting materials were prepared by modified literature procedures (2-vinylpyrrole [13], 2-allylpyrrole [14], $(Et_2BH)_2$ [15], 1,2:1,2-bis(1,4-butane-diyl)diborane(6) [16], $(9\text{-BBN})_2$ [17], N-trimethylsilyl-μ-aminodiborane(6) [8], Et_2O–BH_2Cl [18], N-pyrrolylborane-THF-adduct, N-2,5-dimethylpyrrolylborane-THF-adduct, indolyl-borane-THF-adduct [4,7], 1,2-dithexyldiborane(6) [19]). Mass spectra (EI-MS; 70 eV) were recorded with a VARIAN-MAT CH 7 instrument with direct inlet. NMR spectra were recorded by using Jeol EX270 (^1H, ^{13}C) and Bruker ARX 250 and AM 500 spectrometers (^1H, ^{11}B, ^{13}C, ^{14}N, ^{29}Si). Chemical shifts are given with respect to Me_4Si [$\delta^1H(CHCl_3/CDCl_3) = 7.24$, $(C_6D_6) = 7.15$; $\delta^{13}C(CDCl_3) = 77.0$, $(C_6D_6) = 128.0$; $\delta^{29}Si = 0.0$], Et_2O–BF_3 [$\delta^{11}B$ with $\Xi(^{11}B) = 32.083971$ MHz] and neat $MeNO_2$ [$\delta^{14}N$ with $\Xi(^{14}N) = 7.223656$ MHz].

4.1. 2-Vinylpyrrole (4)

NaOEt (27 mmol; from 0.67 g of Na with EtOH) was suspended together with 9 g (25.2 mmol) of methyltriphenylphosphoniumbromide in 20 ml of THF. The mixture was stirred at room temperature for 3 h. Then a solution of 2.4 g (25.1 mmol) of pyrrole-2-aldehyde in 10 ml of THF was added dropwise. After the reaction mixture was stirred under reflux for 15 h the THF was removed in vacuo and the residue was suspended in CH_2Cl_2 and filtered. The filtrate was extracted with 50 ml of an $NaHSO_3$ solution (15 g of $NaHSO_3$ in H_2O), 50 ml of an Na_2CO_3 solution (10 g of Na_2CO_3 in H_2O) and 50 ml of H_2O. After that the organic phase was dried over Na_2SO_4, and the solvent was removed in vacuo. Distillation gave 1.63 g (70%) of **4** as a colourless liquid (b.p. 50 °C/0.1 Torr). ^{13}C NMR (C_6D_6; 62.9 MHz): $\delta^{13}C = 130.8$ (C-2); 108.1 (C-3); 109.3 (C-4); 119.4 (C-5); 127.3 (CH); 108.5 (CH_2). ^{14}N NMR (C_6D_6; 18.1 MHz): $\delta^{14}N = -230.7$. ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.48 [br] (NH); 6.32 (dd)

[17.8 Hz] [10.3 Hz] (CH); 6.29 (m); 6.12 (m); 5.00 (d) [17.8 Hz], 4.83 (d) [10.3 Hz] (CH_2).

4.2. 2-Allylpyrrole (5)

A mixture of 14 g (0.1 mol) of K_2CO_3 in 70 ml of H_2O, 70 ml of toluene, 14 ml (0.2 mol) of pyrrole was heated to 80 °C. With continuous stirring, 17.5 ml (0.2 mol) of allylbromide was added dropwise. After that the mixture was stirred at 80 °C for 15 h. Then the organic phase was separated and the water phase was extracted twice with ether. The combined organic phases were dried with Na_2SO_4 and the solvent was removed in vacuo. Distillation gave 16 g (75%) of **5** as a colourless liquid (b.p. 50 °C/0.1 Torr). ^{13}C NMR (C_6D_6; 62.9 MHz): $\delta^{13}C$ = 136.5 (C-2); 106.0 (C-3); 108.4 (C-4); 117.0 (C-5); 32.3 ($-CH_2$); 136.3 (CH); 115.9 ($=CH_2$). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$ = 6.14 (m); 5.94 (m); 6.34 (m); 3.05 (d) [6.3 Hz] (CH_2); 5.73 (m) (CH); 4.97 (m) ($-CH_2$); 7.14 [br] (NH).

4.3. Adducts 3a-azonia-3-borata-1,2,3,4-tetrahydropentalenes 6, 7 and 7a-azonia-7-borata-4,5,6,7-tetrahydro-1H-indenes 12–14

4.3.1. General procedure

The respective boron hydride (25 mmol) was dissolved in 30 ml of THF. Then the solution was cooled to −78 °C, and a solution of 25 mmol of **4** or **5** in 20 ml of THF was added dropwise. After warming the reaction mixture to room temperature, stirring was continued for 2 days (in the case of the preparation of **13** under reflux). The solvent was removed in vacuo and the residue was distilled. The compounds **7** and **14** were purified by recrystallisation from hexane.

6: 2.6 g (65%) of a colourless oil (b.p. 88 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.66 (m) (H-5); 5.86 (m) (H-6); 3.59 (m) (HA); 2.44 (m) (H-1); 1.04 (t) [7.4 Hz] (H-2); 0.88 (t) [8.1 Hz] (CH_3); 0.53 (q) (B–CH_2).

7: 4.6 g (85%) of colourless platelets (m.p. 92 °C). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.57 (m) (H-5); 5.82 (m) (H-6); 3.98 (m) (HA); 2.58 (m) (H-1); overlapping multiplets at 2.48–2.08 (cyclooctane-diyl group); 1.48 (t) [7.4 Hz] (H-2); 1.09 (m) (cyclooctane-diyl group).

12: 3.1 g (70%) of a colourless oil (b.p. 102 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.27 (m) (H-3); 4.17 (m) (H-1); 2.39 (m) (HA); 1.53 (m) (H-5); 0.69 (t) [7.1 Hz] (CH_3); 0.46 (m) (H-6); 0.31 (q) (B–CH_2).

13: 1.7 g (40%) of a colourless oil (b.p. 93 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.69 (m) (H-2); 5.87 (m) (H-3); 4.04 (m) (H-1); 2.27 (m) (HA); 1.65 (m) (H-3′/4′); 0.56 (m) (H-6); 0.39 (m) (H-2′/5′).

14: 5.4 g (95%) of colourless platelets (m.p. 83 °C). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.49 (m) (H-2); 5.74 (m) (H-3); 4.36 (m) (H-1); 2.70 (m) (H − 4); overlapping multiplets at 2.42–1.80 and 1.0 (cyclooctane-diyl group and H-6).

4.4. Bicyclic N-pyrrolylboranes 3a-aza-3-bora-1,2,3,3a-tetrahydropentalenes 9–11 and 7a-aza-7-bora-4,5,6,7-tetrahydro-7aH-indenes 17–20

4.4.1. General procedure

The respective boron hydride (25 mmol) was dissolved in 30 ml of THF. After the solution was cooled to −78 °C a solution of 25 mmol of **4** or **5** in 20 ml of THF was added dropwise. In the case of the preparation of **20**, 50 mmol of **5** in THF was added. After warming the reaction mixture to r.t. stirring was continiued for 2 days. Then the solvent was removed in vacuo and the residue was distilled.

9: 2.0 g (43%) of a colourless oil (b.p. 63 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.97 (d) [3.0 Hz] (H-4); 6.45 (t) [3.0 Hz] (H-5); 5.96 (m) (H-6); 2.52 (m) (H-1); 1.53 (m) (H-2); 1.88 (septet) [6.8 Hz] (CH/thexyl group); 0.97 (s) (CH_3); 0.78 (d) (CH_3).

10: 1.5 g (35%) of a colourless oil (b.p. 118 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.92 (m) (H-4); 6.42 (m) (H-5); 5.92 (m) (H-6); 2.76 (m) (H-1); 1.86 (m) (H-2); 7.10 (s) (CH–N/pyrrolyl group); 6.32 (s) (CHCH–N/pyrrolyl group).

11: 1.9 g (35%) of a colourless oil (b.p. 160 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.52 (m) (H-5); 6.04 (m) (H-6); 2.53 (m) (H-1); 2.42 (m) (H-2); 3.45 (t) [8.5 Hz] (N–CH_2); 1.36 (t) (N–CH_2–CH_2); all other signals are overlapping multiplets between 6.7 and 7.5.

17: 3.8 g (74%) of a colourless oil (b.p. 75 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.15 (d) [2.5 Hz] (H-1); 6.18 (t) (H-2); 5.93 (m) (H-3); 2.54 (t) [6.0 Hz] (H-4); 1.53 (m) (H-5); 1.21 (t) [6.3 Hz] (H-6); 2.01 (m) (CH/thexyl group); 0.95 (s) (CH_3); 0.75 (d) [6.8 Hz] (CH_3).

18a: 3.2 g (70%) of a colourless oil (b.p. 130 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.14 (d) [1.9 Hz] (H-1); 6.33 (t) (H-2); 6.01 (m) (H-3); 2.42 (t) [5.9 Hz] (H-4); 1.40 (m) (H-5); 1.11 (t) [6.6 Hz] (H-6); 7.08 (m) (N–CH/pyrrolyl group); 6.41 (m) (N–CHCH/pyrrolyl group).

18b: 4.2 g (79%) of a colourless oil (b.p. 103 °C/0.1 Torr). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.75 (d) [2.2 Hz] (H-1); 6.24 (t) (H-2); 6.07 (m) (H-3); 2.63 (t) [6.1 Hz] (H-4); 1.65 (m) (H-5); 1.31 (t) [7.3 Hz] (H-6); 6.12 (s) (C=CH/2.5-dimethyl-pyrrolyl group); 2.13 (s) (CH_3).

19: 0.8 g (20%) of a light yellow wax (m.p. 50 °C; b.p. 53 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 7.02 (m) (H-1); 6.13 (m) (H-2); 5.88 (m) (H-3); 2.38 (m) (H-3); 1.63 (m) (H-5); 1.40 (m) (H-6).

20: 1.3 g (25%) of a colourless oil (b.p. 75 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.74 (m) (H-1); 6.38 (m) (H-2); 6.13 (m) (H-3); 2.70 (t) [6.1 Hz] (H-4); 1.72 (m) (H-5); 1.13 (t) [6.6 Hz] (H-6); 0.25 (s) (SiCH_3); 3.33 [br] (NH). EI-MS: m/z (%) = 206 (83) [M^+]; 191 (40) [$M^+ - Me$]; 134 (100) [$M^+ - Me_2SiCH_2$].

4.5. Bicyclic N-pyrrolylboranes 8, 15 and 16

4.5.1. General procedure

The respective borata bicycle **6**, **12** or **13** was heated to 80 °C, 100 °C or 130 °C for 15 min. Then fractional distillation gave the pure compounds **8**, **15** or **16**.

8: 2.4 g (72%) of a colourless oil (b.p. 52 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.77 (m) (H-4); 6.45 (t) [2.9 Hz] (H-5); 5.97 (m) (H-8); 2.51 (m) (H-1); 1.41 (m) (H-2); 1.13 (q) [7.5 Hz] (B–CH_2); 0.99 (t) (CH_3).

15: 3.1 g (85%) of a colourless oil (b.p. 65 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.83 (dd) [3.1 Hz] [1.3 Hz] (H-1); 6.21 (t) (H-2); 5.97 (dd) (H-3); 2.57 (t) [12.6 Hz] (H-4); 1.56 (quintet) (H-5); 1.12 (m) (H-6/B-CH_2); 0.98 (t) [6.9 Hz] (CH_3). EI-MS: m/z (%) = 147 (85) [M^+]; 118 (100) [$M^+ - Et$].

16: 0.7 g (15%) of a colourless oil (b.p. 95 °C/0.1 Torr). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 6.83 (m) (H-1); 6.20 (m) (H-2); 5.96 (m) (H-3); 2.58 (m) (H-4); overlapping multiplets at 2.16–0.90 (H-5/H-6/^{n}Bu).

Acknowledgements

The support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Professor Dr. R. Köster, Mühlheim a.d. Ruhr, for a generous gift of triethylborane.

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