Application of ¹¹B NMR spectroscopy to the study of the reactivity of *ortho* substituted anilines with BH₃.THF—I. Formation reactions of new boron heterocycles

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Abstract—The existence of various intermediates in the formation of some boron heterocycles was revealed by ¹¹B NMR spectroscopy. The structure of these intermediates was established by comparing them with model compounds. Four new boron heterocycle compounds bearing a hydride function and three new spiroborates with catechol and *ortho* substituted anilines as ligands were prepared. The structures were established by spectroscopic measurements.

INTRODUCTION

As a part of our research program on the reactions of borane with bifunctional compounds [1-2], we report here the analysis of the reaction of *o*-substituted anilines 1-4 with borane. We describe the synthesis of a series of new boron heterocycles bearing one hydride function 5-8. Also we report here the intermediates observed by ¹¹B NMR which are formed during the synthesis and the reactivity of heterocycles 5-8 with phenol, aniline and catechol. Four boron spiroheterocycles 22-25 were obtained as the result of the reaction of catechol with compounds 5-8 or from the reaction of catecholborane with compounds 1-4.



EXPERIMENTAL

¹¹B NMR spectra were measured at 32.1 MHz in the FT mode using a Varian XL-100A spectrometer. Sample tables of 10 mm o.d. were used and the temperature in the probe was 32.5° C. ¹¹B chemical shifts are given in ppm as positive values to high frequency (low field) relative to external BF₃.OEt₂. Preparation of BH₃.THF was performed according to the literature [3]. The concentration of BH₃.THF was 2.18 M. All the compounds were purified by distillation from a drying agent under an inert atmosphere. The reactions were carried out under a dry nitrogen atmosphere. Nitrogen purged, oven dried hypodermic syringes fitted with stainless steel were used to fill the NMR tubes. ¹H NMR spectra were recorded on a Varian EM-390 spectrometer using tetramethylsilane as an internal standard. Mass spectra were measured at 70 eV on a

Hewlett Packard 5985-A instrument and i.r. spectra were recorded on a Nicolet MX-1 FT-IR spectrometer.

RESULTS AND DISCUSSION

¹¹B and ¹H chemical shifts for the borane compounds identified in this study are given in Tables 1, 2 and 3. Infrared data, mass spectra and melting points of isolated compounds are in Tables 4, 5 and 6. All the *o*-substituted anilines were made to react with borane in (1/1) and (2/1) (aniline/borane) ratios and the reactions monitored by ¹¹B NMR.

1. Reaction of o-aminophenol 1 with BH₃.THF

1.1. o-Aminophenol/borane (1/1.1) molar ratio*. To 1.0 equivalent of o-aminophenol 1.1 equivalents of BH₃.THF were added. Five minutes at 33°C after the reaction had started, the NMR spectrum consisted mainly of a quartet at -17 ppm while a doublet at + 28 ppm was slowly starting to show. Identification of the first signal can be easily made by analogy with aniline borane ($\delta = -17 \text{ ppm } [4]$) and attributed to amine boron adduct formation. Thirty minutes later the only signal that remained was the doublet at +28 ppm (J = 168 Hz). The latter was attributed to the heterocycle with a > B-H function 5 since its chemical shift and coupling constant are comparable to the catecholborane 9 known in the literature [5, 6]. Due to the fact that compound 5 decomposes on evaporation to dryness it was not isolated but characterized in solution (Table 4).



*The equimolar ratio gave a mixture of compounds at the end of the reaction.

Table 1. ¹¹B and ¹H NMR data

		s ¹¹ B ppm	J (¹¹ B ¹ II) *T	$HF(BF_{3}OEt_{2}) \delta^{1}H ppm CC1_{4}(TMS)$	
5		+28	168		
<u>6</u>		+28	170	$\begin{array}{cccc} 7,25 & (5H) & -C_{c}H_{c} \\ 6,67-7.0 & (4H)^{9.5}C_{6}H_{d} \\ 4.85 & (2H) & -GH_{2} \end{array}$	
18	S BH2	-8.5	113		
7	S BH	+3?	156	6.9-7.2 (21) aromatic 7.5-7.7 (21)	
8	MI_BH	+23	134	6.8-7.2 (401) aromatic	
9		+26	188		

*Solvent and reference.

Table 2. ¹¹B NMR data



*Ref. [4a].

**Solvent and reference.

It is remarkable that in spite of the fact that the cyclic structure with the $-BH_2$ function should be an intermediate (Fig. 1), the corresponding signal in ¹¹B NMR is not seen for the *o*-aminophenol, indicating that we are dealing with a short-lived species.

1.2. o-Aminophenol/borane (2/1) molar ratio. To 1.0 equivalent of o-aminophenol 0.5 equivalent of BH₃.THF was added. The spectrum was recorded immediately (5 min, 33° C) showing signals at -17, +7

and + 24 ppm. One of the first signals to show up was the broad line centered at -17 ppm. The reaction was allowed to reach equilibrium by standing 30 min at 40°C or 20 min at 70°C. At that time the spectrum consisted solely of the signals at + 7 and + 24 ppm in equal proportion. These signals were identified by separate experiments (see below). The singlet at + 7 ppm was attributed to structure 10 and the signal at + 24 was attributed to either structure 11 or 12.



1.3. Reactions of heterocycle 5 with phenol and aniline. The first experiment consisted of adding to a pure solution of 5 in THF 1.0 equivalent of phenol at 25° C. Two signals were observed in the spectrum, the

doublet at +28 ppm corresponding to 5 and a singlet at +7 ppm attributed to 13, both signals having the same area (Fig. 2b). On heating to 45°C for 15 min the signals at +7 and +28 ppm diminish very slowly and



Fig. 1. Reaction mechanism proposed for 1-4 with BH₃.THF.



Fig. 2. ¹¹B NMR spectra of the reaction of 5 with phenol. (a) Compound 5. (b) Addition of 1.0 equivalent of phenol 25°C, 5 min. (c) Heating to 45°C, 15 min. (d) Addition of a second equivalent of phenol.

Table 3. ¹¹B and ¹H NMR data

	δ ¹¹ Bppm	$\texttt{J(}^{11}\texttt{B}-^{1}\texttt{H}\texttt{)}\texttt{THF}(\texttt{BF}_{3}\texttt{OEt}_{2})^{\star\star} \&^{1}\texttt{H} \texttt{ ppm } \texttt{DMSO}(\texttt{TMS})^{\star\star}$
	+14	6.5(s)(4H) 6.55-7(m)(4H) 9.8(b)(2H)
$\underline{23} \qquad \underbrace{0}_{H} \underbrace{0}_{N} \underbrace{0}_{H} \underbrace{0}_{M} \underbrace{0}_{H} \underbrace{0}_{M} \underbrace{0}_{H} \underbrace{0}_{M} \underbrace{0}_{H} \underbrace{0}_{M} $	+14 r	4,42(s)(1H)4,68(s)(1H) 7,31(s)(2H) 6,52(s)(4H) 7,4(s)(3H) 6,58-7,15(m)(4H) 10,2(b)(1H)
	+14	6.5(s)/4H) 6.53-7.3(m)(4H) 7.9(s)(2H)
$\frac{25}{0} \bigcirc 0 = B < N = 0$	+14	6.5(s)(4H) 6.52-6.98(m)(4H) 3.5(b)(7H) 8.8(b)(1H)
9 0 BH	+26	188 0.9*(m)
$\underline{26}$ $\underline{\bigcirc}$ $\underline{\frown}$ $\underline{\bigcirc}$ $\underline{\bigcirc}$ $\underline{\frown}$ $\underline{\bigcirc}$ $\underline{\frown}$ $\underline{\frown}$ $\underline{\frown}$ $\underline{\bigcirc}$ $\underline{\frown}$		6.7(m)(4H) 8.8(s)(2H)
		4.5(b)(2H) 6.5-6.8(m)(4H) 8.85(b)(1H)
		4,3-4,34(d)(2H) 5,2(t)(1H) 6,3-6,9(m)(4H) 7,4(s)(5H) 9,3(s)(1H)
3 O SI MI2		4.86(b)(3H) 6.3-7.3(m)(3H)
4 Or MI2		1,1 (s)(4n) 6,45(m)(4H)

*In CDCl₃. **Solvent and reference.

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			О-В	N-B	.N_⇒B (cmr-1)	B-14	N-H
<u>5</u>		ŤHF	1335,1310	1442		2609	3334
<u>6</u>		THF CC1 KBr ⁴	1350 1375 1388,1351	1400 1450 1474		2609 2609 2625	
<u>18</u>	S BIL2	kB r			1100	2460 2370	3376 3369
7_	S BH	THI				2600	3 300
<u>8</u>		Т НЕ		1450		2577	3380
<u>9</u>	D BH	THF	1350			2651	

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Table 5. Infrared and m.p. data

Table 6. Mass spectrum data m/e (relative intensity)* and m.p. data



**The dimer (234) was also observed.

are replaced by a simple broad signal at + 24 ppm that predominates, 14 (Fig. 2c).

The addition of a second equivalent of phenol to this solution causes the signal at +7 ppm to predominate, 13 (Fig. 2d). By phenol precipitation the signal at +24 ppm increases again indicating the existence of equilibrium. By analogy, structure 10 was found comparable to 13. The observation of the addition reaction of an -OH bond to the B-N bond that transforms the σ N bond into a coordination NH \rightarrow B bond is a remarkable fact.

It was impossible to distinguish by ¹¹B NMR the two structures **11** and **12** since for the analogous compounds **15** and **16** a single chemical shift at +25 ppm is reported in the literature [7].



In order to have more information about species 11 and 12, we decided to add aniline to 5. A coordination reaction was expected (Fig. 3), but none was observed. However, the addition of 1.0 mole of aniline to a solution containing basically 14 showed a sensible shift from equilibrium and the increase of the signal at +7 ppm. This suggests that aniline is also involved in the equilibrium (Fig. 4).

1.4. Reactions of heterocycle 5 with catechol. Addition of 1.0 equivalent of catechol to a solution of 5 in THF results in a unique, sharp signal at + 14 ppm; the structure of this product is discussed in Section 5.

1.5. Reversibility of the reaction equilibria in the presence of BH_3 .THF. A demonstration that products 5, 10, 11 and 12 are chemical species in equilibrium is that



Fig. 3. Assumed coordination reaction of aniline to 5; this reaction was not observed by ¹¹B NMR.



Fig. 4. Equilibrium proposed between 14 and aniline.

the addition of an excess of BH_3 .THF makes these species disappear first in favor of a signal at -17 ppm and then the doublet at +28 ppm; finally the heterocycle 5 is the only species observed. Once more the addition of *o*-aminophenol to this solution brings out the products 10, 11 and 12 observed before. The mechanism by which these transformations occur are most likely based on bond interchanges between boron-oxygen and boron-nitrogen with boron-hydrogen bonds. A possible mechanism is shown in Fig. 5.

2. Reaction of N-benzil-o-aminophenol 2 with $BH_{\rm 3}, THF$

2.1. N-benzil-o-aminophenol/borane in equimolar ratio. To 1.0 equivalent of N-benzil-o-aminophenol we added 1.0 equivalent of BH₃.THF; after 5 min at 33°C, we observed a broad singlet centered at -12 ppm and the origin of an underdefined doublet at +28 ppm. After 2.5 h at 20°C the doublet at +28 ppm (J = 170 Hz) is the only signal observed. The signal at -12 ppm can be attributed to a boron adduct of a secondary amine [4a] (Table 2). The doublet at +28 ppm (J = 170 Hz) can be attributed to heterocycle 6. Isolation of compound 6 was easily made. It is a white crystalline compound, m.p. 60°C.

2.2. N-benzil-o-aminophenol 2 with BH_3 . THF in (2/1) molar ratio. Compound 6 was the only product ob-



Fig. 5. Equilibrium reactions proposed between compound 10 and borane.

served at the end of this reaction. The analogous species to 10, 11 and 12 were not observed.

2.3. Reactions of heterocycle 6 with phenol, aniline and catechol. Compound 6 did not show reactivity at 25°C either with phenol or aniline. It is noteworthy that alkyl substitution on the amine stabilizes the heterocycle 6. With catechol a fast reaction gave only one product with a $\delta = +14$ ppm (see Section 5).

3. Reaction of o-aminothiophenol 3 with BH₃.THF

3.1. o-Aminothiophenol/borane in equimolar ratio. Substitution of oxygen by sulphur produces a variation in the behavior of ortho substituted aniline. To 1.0 equivalent of o-aminothiophenol 3, 1.0 equivalent of BH₃.THF was added and two signals were immediately observed (1 min at 33°C): a quartet at -17 ppm (J = 93 Hz) plus a triplet at -8.5 ppm (J = 113 Hz). After 10 min at 20°C only the triplet and a small doublet at +37 ppm (J = 156 Hz) were observed. After 12 h at 20°C only the doublet was observed. It is rather interesting that in this case a triplet was observed. It is attributed to a $-BH_2$ function, but it was necessary to distinguish between two possibilities 17 and 18. This ambiguity could be



easily solved by a separate experiment: reaction of thiophenol with BH₃.THF produces a triplet $\delta = +4$ ppm (J = 107 Hz). It is known that the arylthioboranes coordinate within themselves through the formation of trimers or dimers [8], which expalins the shifting of the signal to higher fields. The addition of aniline to this arylthioborane shows a broad signal at -8.5 ppm. This shift indicates that there is coordination with the aniline 19. This experiment supports the structure 18 for the signal at -8.5 ppm. The doublet at +37 ppm was attributed to the heterocycle with a > BH function 7. This heterocycle is remarkably stable, as it can be isolated without decomposition as a crystalline compound, m.p. 52°C.

3.2. o-Aminothiophenol 3 with BH₃.THF in (2/1) molar ratio. Only compound 7 was obtained from this reaction.

3.3. Reactions of heterocycle 7 with phenol, thiophenol, aniline and catechol. Compound 7 did not show reactivity with thiophenol or aniline but with one equivalent of phenol it gave a simple signal at +35 ppm attributed to structure 20. The reaction of addition of 2.0 equivalents of phenol was not observed. Reaction of 7 with catechol gives a unique, sharp signal at + 14 ppm (see Section 5).



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4. Reaction of phenylenediamine 4 with BH₃. THF

4.1. Phenylenediamine/borane in equimolar ratio. Investigation of the phenylenediamine reaction led to the following results: we added 1.0 equivalent of BH₃.THF to phenylenediamine 4; after 15 min at 33°C, we observed a quartet at -18 ppm (J = 85 Hz) and the formation of a doublet at +23 ppm (J = 134 Hz). After 50 min at 40°C the relative areas of the quartet and the doublet were 1:1. After 4 h of heating the only signal that could be observed was the doublet at +23 ppm. This was attributed to the heterocycle 8.

4.2. Phenylenediamine 4 with BH_3 . THF in (2/1) molar ratio. Only compound 8 was observed at the end of this reaction.

4.3. Reactions of heterocycle 8 with phenol, aniline and catechol. The heterocycle 8 of stable nature did not show reactivity with aniline, but with phenol gives a simple signal at +24 ppm that is attributed to structure 21. Reaction of 8 with catechol gives a unique sharp signal at +14 ppm (see Section 5).



5. Reactivity of 5, 6, 7, 8 with catechol

Addition of catechol to heterocycles 5–8 gave in all cases a crystalline product soluble in DMSO, which gave in ¹¹B NMR a sharp singlet at + 14 ppm. These signals were attributed to bicyclic compounds, 22, 23, 24, 25. The same spiroboranes 22–25 were obtained in the addition of *ortho* substituted anilines 1–4 to the catecholborane 9. Spectral data for compounds 22–25 (Tables 3 and 5) were in good agreement with the proposed structures* (Fig. 6). Infrared spectra showed the presence of a B–O vibration at 1490 cm⁻¹ a B–N vibration between 1060 and 1375 cm⁻¹ and the absence of –BH, –OH or –SH absorptions. As expected for a tetrasubstituted boron atom with a nitrogen coordination, the chemical shift of the spiroboranes 22-25 appears at low field (+14 ppm) with respect to tricoordinated molecules 12, 20 and 21 (Table 2).

It is known from ¹H NMR spectra that aromatic protons shift to high field when the donor character of substituents increases. In catecholborane 9 the oxygen-boron electronic retrocoordination decreases the electronic donation from the oxygen to the aromatic ring and the aromatic protons are shifted to lower fields. In the spiroborates 22, 23, 24 and 25, the aromatic protons of catechol appear again at high field due to the $N \rightarrow B$ coordination that reduce the capability of oxygen-boron electronic retrocoordination and allow the electrons on oxygen to delocalize into the aromatic ring (see Table 3).

CONCLUSION

Several new heterocycles of boron 5–8, 10, 13, 14, 18, 20, 21, 23, 24 and 25 were characterized by ¹¹B NMR spectroscopy and some of them were isolated: 6–8, 18, 23–25.

Formation of 5 from o-aminophenol is not a simple reaction; some intermediates were observed and characterized. A demonstration was given that these systems are in equilibrium and that the reaction products depend on reagent concentration.

It is noteworthy that the existence of an addition reaction of an -O-H bond to the N-B bond allows the change of a σ N-B bond to a coordination N \rightarrow B bond. This phenomenon was observed in the reaction of Fig. 2 and in the formation of spiro compounds derived from heterocycles 5-8 and catechol (Fig. 6). Compounds 6, 7 and 8 did not show the addition of two phenols as was observed in heterocycle 5.

The normal reaction of ligands 2-4 with borane seems to be the one depicted in Fig. 1. Formation of aniline borane adducts was observed in all cases as a previous reaction.

The ArXBH₂ (X = O, N, S) compounds are, in general, unstable to disproportionation but in some exceptional cases they can be isolated [1, 2]. In this work it is remarkable that for ligands 1, 2 and 4 the intermediates of structure 26 were not observed, even as fugacious species. Surprisingly, for ligand 3 this structure was stable enough to be observed and isolated 18.



Catechol reactions with heterocycles 5–8 gave spiromolecules 22–25 that showed a great stability. In these reactions the amino function changes to an amine-boron coordination bond. The same products

^{*}The compound 22 has been previously reported in the literature, but no spectroscopic data were given in support of its structure [9].



 1 of 3 = 0 X = 0 R = n 22 X = 0 R = n

 2 or 6 X = 0 $R = -CH_2C_6H_5$ 23 X = 0 $R = -CH_2C_6H_5$

 3 or 7 X = S R = H 24 X = S R = H

 4 or 8 X = NH R = H 25 X = NH R = H

Fig. 6. Scheme of the two different reactions of synthesis of spiroborates 22-25.

could be obtained from catecholborane and ligands 1-4.

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