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^{11}B Nuclear magnetic resonance study of the reactivity of borane tetrahydrofuran with representative dithianes, diazolidines, thiazolidines, benzothiazolines and benzothiazoles

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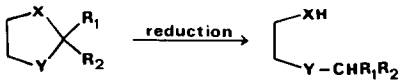
Abstract—The reaction of borane tetrahydrofuran with the title compounds led by ring opening to the synthesis of new borolidine heterocycles. ^{11}B NMR not only allowed the observation of borane adducts of dithianes, diazolidines, thiazolidines, benzothiazolidines and benzothioles, but even provides useful information concerning their stereochemistry.

INTRODUCTION

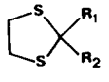
As part of our continuing studies on the reactivity of borane adducts we have examined five-membered ring heterocycles containing sulfur and nitrogen.

It is known that reaction of 1,3-five-membered ring heterocycles with reducing agents affords ring opening products as evidenced by the numerous reports which have appeared in the literature [1–4].

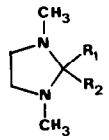


X and Y = S, O or N–R

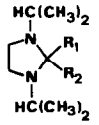
In contrast to these observations, we have found that the reaction of BH_3SMe_2 with oxazolidines under mild conditions prevents ring opening and affords $N \rightarrow BH_3$ adducts that are excellent systems for stereochemical studies [5–6]. Based on the previous results we decided to extend our research to other heterocycles containing sulfur and nitrogen with the aim of obtaining mono- and diadducts of borane as well as knowing their stereochemistry and investigating the reaction conditions and structural features that favor ring opening. We have done a ^{11}B NMR study of ring substituent effects on the reactivity of BH_3THF with the dithiolanes **1a–1b**, diazolidines **7a–17a**, thiazolidines **18a–25a**, benzothiazolidines **26a–29a** and benzothiazoles **30a–32a** (Scheme 1).



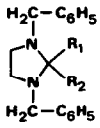
1a $R_1 = R_2 = H$
2a $R_1 = H$ $R_3 = CH_3$
3a $R_1 = H$ $R_2 = C_6H_5$
4a $R_1 = R_2 = CH_3$
5a $R_1 = CH_3$ $R_2 = C_6H_5$
6a $R_1 = R_2 = C_6H_5$



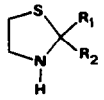
7a $R_1 = R_2 = H$
8a $R_1 = H$ $R_2 = CH_3$
9a $R_1 = H$ $R_2 = C_6H_5$
10a $R_1 = R_2 = CH_3$
11a $R_1 = CH_3$ $R = C_6H_5$



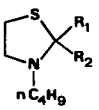
12a $R_1 = R_2 = H$
13a $R_1 = H$ $R_2 = CH_3$
14a $R_1 = H$ $R_2 = C_6H_5$



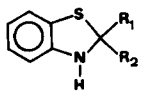
15a $R_1 = R_2 = H$
16a $R_1 = H$ $R_2 = CH_3$
17a $R_1 = H$ $R_2 = C_6H_5$



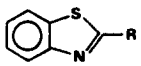
18a $R_1 = R_2 = H$
19a $R_1 = H$ $R_2 = CH_3$
20a $R_1 = H$ $R_2 = C_6H_5$
21a $R_1 = R_2 = CH_3$



22a $R_1 = R_2 = H$
23a $R_1 = H$ $R_2 = CH_3$
24a $R_1 = H$ $R_2 = C_6H_5$
25a $R_1 = R_2 = CH_3$



26a $R_1 = R_2 = H$
27a $R_1 = H$ $R_2 = CH_3$
28a $R_1 = H$ $R_2 = C_6H_5$
29a $R_1 = R_2 = CH_3$



30a $R = H$
31a $R = CH_3$
32a $R = C_6H_5$

Scheme 1.

EXPERIMENTAL

^{11}B NMR spectra were recorded on Varian XL-100A (32.1 MHz) and a Jeol FX-90Q (28.69 MHz) while ^1H NMR spectra were obtained with a Varian EM-390 spectrometer. Chemical shifts are given in ppm relative to BF_3Et_2O and TMS.

Tetrahydrofuran was distilled from $LiAlH_4$ under dry N_2 prior to utilization, the borane–THF complex was prepared using a published procedure [7]. Reactions were carried out under a nitrogen atmosphere. The preparation of dithianes [8–10], diazolidines [11], thiazolidines [12], benzothiazolines [13] and benzothiazoles [14, 15] has been described elsewhere.

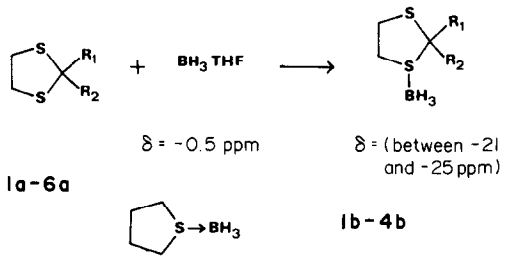
One or two equivalents of BH_3THF were added to compounds **1a–32a** in order to obtain mono- or diborane adducts following the general procedure below. To a stirred

solution containing 10 mmol of the heterocycle in 4 ml of THF and cooled using a dry-ice–acetone mixture was added dropwise a solution of 2.0 M BH_3THF in THF (10 mmol for monoaddition and 20 mmol for diaddition, respectively). Immediately after addition, a ^{11}B NMR spectrum was obtained and the reaction course followed by recording spectra at successive intervals. Attempts to isolate the reaction products were in many cases unsuccessful due to their relative stability and sensitivity to oxygen and moisture. Therefore in general the products were directly studied in THF solution, except for some diazolidines N–BH_3 adducts where $CDCl_3$ was added after evaporation of THF in order to get ^{1}H NMR spectra.

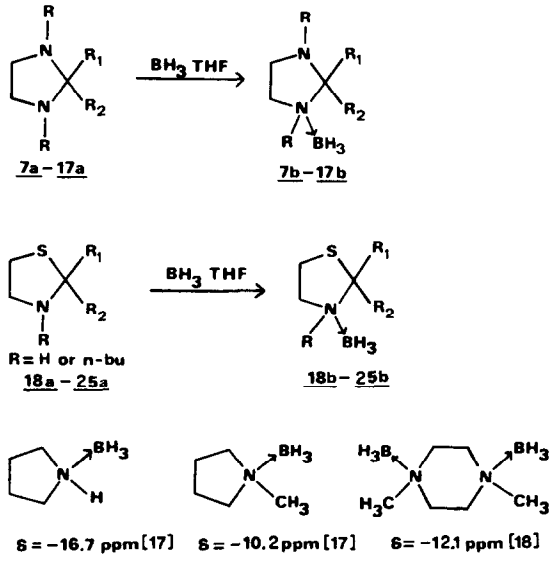
RESULTS AND DISCUSSION

Formation of monoadducts

Compounds **1a–4a** gave partial formation of S–BH_3 adducts as evidenced by the appearance of the signal at approximately $\delta = -20$ ppm characteristic for *S*-borane adducts [16] (Table 1). Compounds **1b–4b** are weak adducts which decompose upon evaporation to dryness.



Compounds **5a** and **6a** were not basic enough to form adducts; this can be attributed to disubstitution at C_2 where one of the groups is a phenyl.



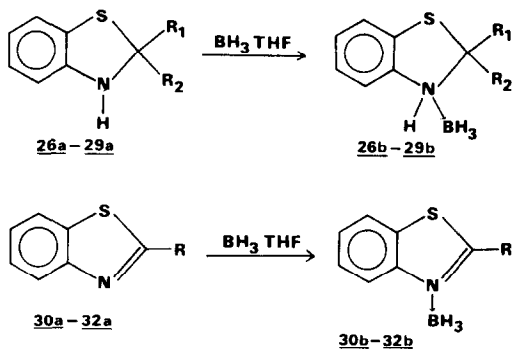
Diazolidines **7a–17a** and thiazolidines **18a–25a** afforded the *N*-monoborane adducts as deduced from the ^{11}B NMR data (Table 1) which are in good agreement with values reported for similar *N*-borane heterocycles [18]. The structures and nitrogen configurations of **7b–12b**, **13b**, **15b** and **17b** were also established from ^{1}H NMR (Table 2).

Table 1. ^{11}B NMR data of monoborane adducts **1b–32b**

Compound	^{11}B$\delta^*(J_{B-H})$	Compound	^{11}B$\delta^*(J_{B-H})$
1b†	−22.0 (117)	**17b**	−11.8‡
2b†	−22.5 (102)	**18b**	−17.0 (98)
3b†	−21.0‡	**19b**	−17.7 (98)
4b†	−25.0‡	**20b**	−17.5 (93)
5b§	—	**21b**	−20.6 (96)
6b§	—	**22b**	−12.1 (99)
7b	−10.0 (99)	**23b**‖	−12.5 (96) −15.0‡
8b‖	−11.0 (99) 80% −12.5 (100) 20%	**24b**	−12.6 (91)
9b	− 9.9 (98)	**25b**§	—
10b	−13.3 (99)	**26b**	−16.2 (73)
11b	−13.5 (97)	**27b**‖	−16.6‡ (90) −20.0‡ (10)
12b	−14.0 (98)	**28b**	−18.1‡
13b‖	−13.2 (96) −18.7¶ (94)	**29b**	−21.1‡
14b‖	−14.1 (98) 90% −18.6‡ 10%	**30b**	−17.1 (91)
15b	−10.7 (92)	**31b**	−20.0 (98)
16b	−12.1 (92)	**32b**	−18.0 (95)

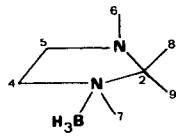
*In THF δ in ppm and J in hertz, $BF_3 \cdot OEt_2$ as internal reference.
†*S*-Borane adduct was formed partially.
‡Unresolved signals.
§Was not observed.
‖Two isomers observed.
¶After heating this is the only signal that remains.

Although benzothiazolines **26a–29a** and benzothiazoles **30a–32a** also gave *N*-borane monoadducts (Table 1) they are readily transformed into other heterocycles, *vide infra*.



Because of the ability of borane to selectively form stable adducts with the nitrogen atom and fix its configuration, diazolidines **13a**, **14a**, **16a** and **17a**, *N*-borane thiazolidines **19a**, **20a**, **23a** and **24a** and benzothiazolines **27a** and **28a** with different substituents at C_2 can afford stereoisomers which can be distinguished taking advantage of the extreme sensitivity of ^{11}B NMR to steric effect [5, 6].

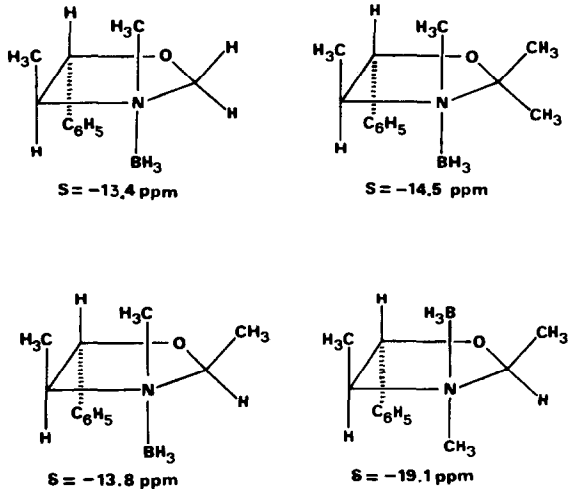
Table 2. ^{1}H NMR data of *N*-borane diazolidines **7b–17b***



Compound	C_2H	C_4HC_5H	C_6HC_7H	C_8H	C_9H
7b	2.65, *s*, 2H	3.2, *m*, 4H	2.4, *s*, 3H 2.8, *s*, 3H		
8b	3.25, *q*, 1H J = 6 Hz	2.7–3.5, *m*, 4H	2.35, *s*, 3H 2.54, *s*, 3H	1.25, *d*, 3H J = 6 Hz	
9b	4.35, *s*, 1H	2.5–3.7, *m*, 4H	2.25, *s*, 6H	7.4–7.6, *m*, 5H	
10b	—	2.4–3.6, *m*, 4H	2.30, *s*, 3H 2.65, *s*, 3H	1.2, *s*, 3H	1.3, *s*, 3H
11b	—	2.4–3.8, m, 4H	2.3, *s*, 6H	1.75, *s*, 3H	7.4–7.8, *m*, 5H
12b	3.35, *d*, 1H J = 7.5 Hz 3.94, *d*, 1H J = 7.5 Hz	2.3–3.4, *m*, 6H isopropyl signals: 1.1, *d*, 6H, J = 6 Hz 1.35, *d*, 6H, J = 6 Hz			
13b	4.2, *q*, 1H	complex signals			
15b	3.4, *d*, 1H J = 6 Hz 3.77, *d*, 1H J = 6 Hz	2.9–3.6, *m*, 4H	3.65, *d*, 2H J = 1.5 Hz 4.10, *d*, 2H J = 1.5 Hz		
17b	5.1, *s*, 1H	complex signals		7.25–8.0, *m*, 15H	

*It was not possible to isolate pure compounds for **14b** and **16b**.

The usefulness of ^{11}B NMR in this respect is evident in the observed chemical shift for the *N*-borane oxazolidines shown in Scheme 2 [5]. Clearly δ reflects whether the borane is in front of a methyl or a proton and the high field shifts indicate steric hindrance.



Scheme 2.

It has been demonstrated that borane addition to these systems is stereoselective and that borane goes to the less hindered position. These observations are also in accordance with the data reported herein (Scheme 3).

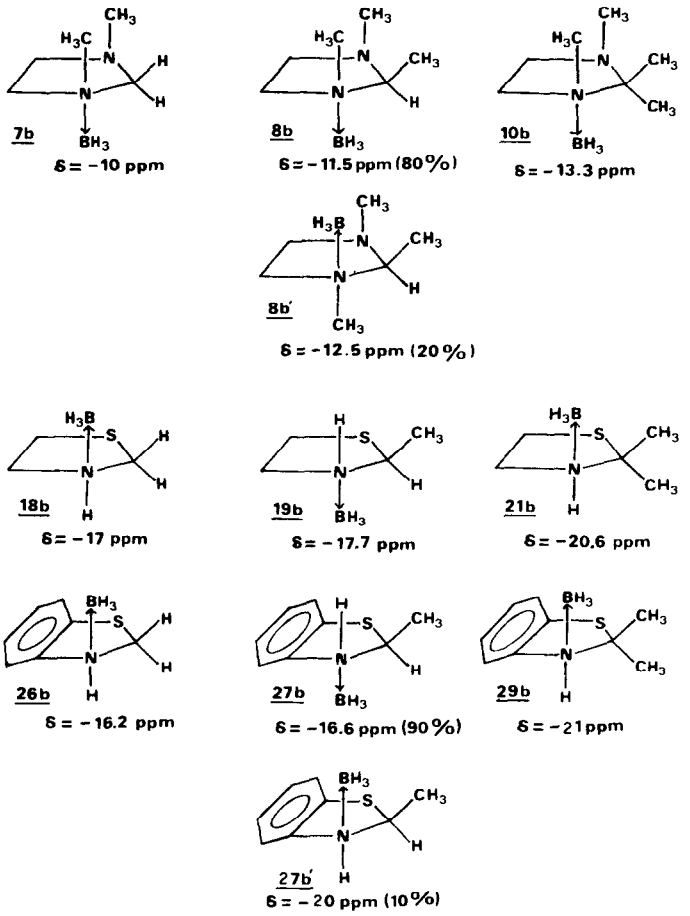
Chemical shifts of derivatives where C_2 is a methylene (**7b**, **18b** and **26b**) are very different from compounds with two methyls at C_2 (**10b**, **21b** and **29b**). Comparison of these compounds with the adducts obtained from heterocycles with one methyl at C_2 clearly shows that mono *N*-boranes obtained for **8b**, **19b** and **27b** were predominantly the isomer with the BH_3 at the less hindered position, *trans* to the substituent in C_2. Only in three cases were the *cis* isomers observed (**8b'**, **13b'** and **14b'**). This disposition prevailed even in heterocycles possessing a bulky substituent at nitrogen as *N*-benzyl or *N*-isopropyl diazolidines (Scheme 4).

Formation of borane diadducts

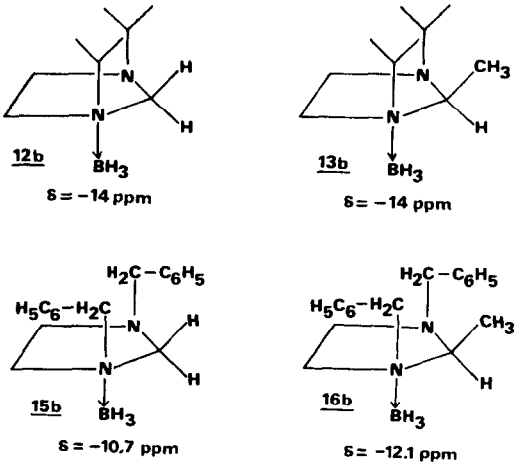
Of all the heterocycles studied, only diazolidines **7a–9a**, **12a**, **13a**, **15a** and **16a** afforded diadducts, and all except for **16c** (Tables 3 and 4) were isolated. Although *N,N*-diborane diazolidines with two identical substituents at C_2 (**7c**, **12c** and **15c**) are capable of affording a couple of enantiomers with the boranes in the *trans* position and one isomer with *cis* boranes, but only one isomer was detected for the mentioned compounds (Scheme 5).

On the other hand when substituents in C_2 are different as in compounds **8c**, **9c**, **13c** and **16c** three isomers (one dl pair with *trans* boranes and two *cis* isomers) are distinguishable in NMR (Scheme 5).

Accordingly, for compounds **8c**, **9c** and **13c**, two different signals were observed in ^{11}B NMR indicating



Scheme 3.

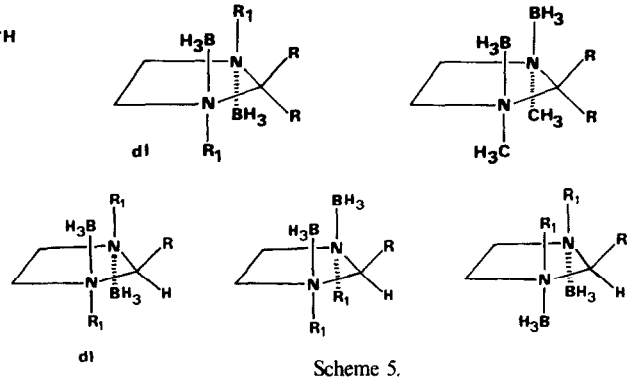


Scheme 4.

Table 3. ^{11}B NMR data of *N,N*-diborane adducts of diazolidines*

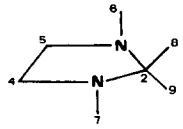
Compound	^{11}Bδ(J_{B-H})	Compound	^{11}Bδ(J_{B-H})
7c	−8.5	13c	−13.2
			−16.0
8c	−8.3	15c	−9.0
	−13.4		
9c	−6.9	16c	−12.0
	−11.2		
12c	−14.1 (J = 104)		

*See footnote, Table 1.



Scheme 5.

Table 4. ^{1}H NMR data of *N,N*-diborane diazolidines*



Compound	C_2H	C_4–H C_5–H	C_6–H C_7–H	C_8–H
7c†	4.1, *s*, 2H	3.6, *s*, 4H	2.95, *s*, 6H	
8c†	4.0, *q*, 1H *J* = 6 Hz	3.0–3.9, *m*, 4H	2.74, *s*, 3H 2.88, *s*, 3H	1.54, *d*, 3H *J* = 6 Hz
9c†	4.9, *s*, 1H	2.9–4.0, *m*, 4H	2.6, *s*, 3H 2.8, *s*, 3H	7.3–8.1, *m*, 5H
12c†	4.18, *s*, 2H	3.25–3.8, *m*, 6H	1.38, *d*, 6H *J* = 6 Hz 1.41, *d*, 6H *J* = 6 Hz	
13c	2.4–4.0, *m*, 7H		1.02–1.3, *m*, 12H	
15c†	4.2, *s*, 2H	3.1–3.9, *m*, 4H	4.25, *s*, 4H	7.2–7.6, *m*, 10H
16c	complex mixture			

*See footnote, Table 1.
†Only one isomer was observed.

either the presence of two species or the *trans* isomer. ^{1}H NMR supports the latter proposition; however, no definitive assignment of structures was attempted.

Ring opening

Some diazolidines gave, after addition of a second equivalent of borane THF, the N → BH_3 coordinated boradiazolidine species (**10d, 11d, 14d, 16d** and **17d**) (Table 5). Each of these compounds exhibited two boron signals with the same integration, one is a triplet showing δ between +2.7 and +5.9 ppm which corresponds to a N–BH_2 ← N function and the other is a quartet for a N–BH_3 group in the range between −9.9 and −18.0 ppm.

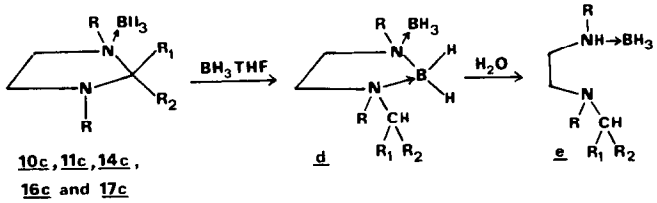


Table 5. ^{11}B NMR data of BH_2 heterocycle borane adducts*

Compound	N → BH_3	N → BH_2–N
10d	−9.9 (98)	+5.5 (112)
11d	−9.6 (93)	+5.9 (94)
14d	−17.2 (93)	+2.7
16d	−18.0	+3.8
17d	−18.0	+5.0
	S → BH_3	N → BH_2–S
18d	−21.0 (104)	−6.5 (110)
19d	−21.0	−8.0
20d	−21.0	−6.1
21d	−20.0	−9.2
23d	−20 (95)	−3.5 (119)
24d	−21.0	−3.7 (116)
25d	−21.0	−4.4 (109)
26d	−20.6	−9.5
28d	—	−4.7 (108)
29d	−21.0	−9.4 (110)
31d	−25.0	−8.0 (148)

*See footnote, Table 1.

The heterocycles marked as *d* possess strong N–B bonds resistant to hydrolysis at room temperature, however at 70°C they afford the N–BH_3 alkylated amines *e* (Table 6).

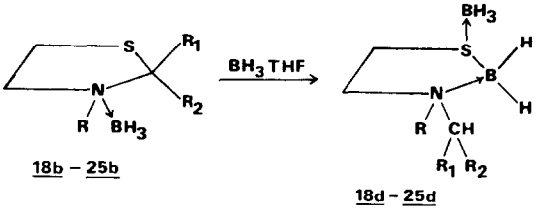
Addition of a second equivalent of BH_3THF to *N*-borane thiazolidine did not afford the diadduct, instead the S–BH_3 coordinated borathiazolidine heterocycles (**18d–21d** and **23d–25d**) were obtained, their

Table 6. ^{11}B NMR data of *N*-monoborane diamines*

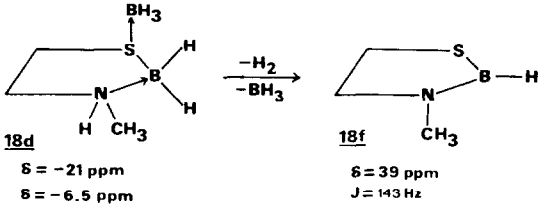
Compound	δ(*J*)
10e	−15 (95)
11e	−14.6 (98)
14e	−19.4
16e	−13.1
17e	−14.5

*See footnote, Table 1.

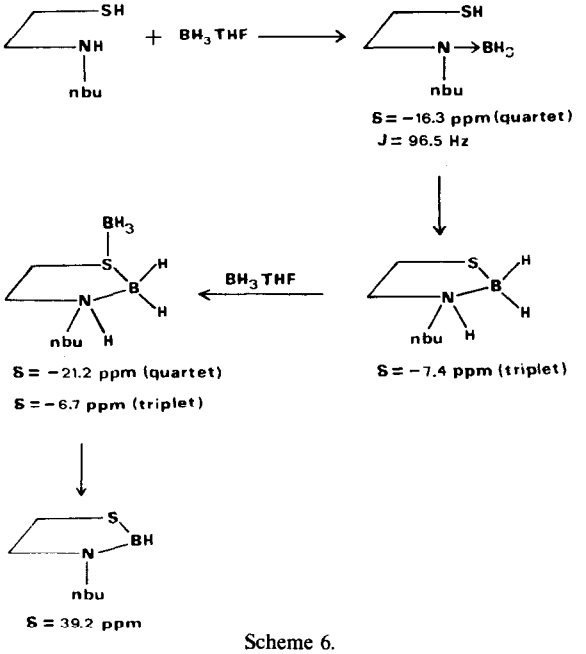
data are in Table 5. The reaction products give a BH_3 signal at high field (between -20 and -21.5 ppm) characteristic of a S → BH_3 group and a triplet (between -3.5 and -9.2 ppm) assigned to a S–BH_2 ← N coordinated species. Compounds **18d–25d** are stable structures that afford the *N*-alkylated aminothiols upon hydrolysis.



Compound **18d** yielded heterocycle **18f** by elimination of a H_2 and a BH_3 molecule.



The assignment of structure for boron heterocycles **18d–25d** can be easily accomplished by comparison with the reaction products of *N*-butyl aminoethanethiol (Scheme 6).



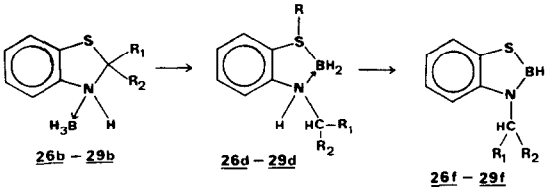
Scheme 6.

Table 7. ^{11}B NMR data of BH heterocycles*

Compound	B–H	Compound	B–H
18f	+39 (143)	**29e**	+36 (166)
26f	+37.5 (156)	**30e**	+37 (135)
27f	+36 (158)	**31e**	+37 (148)
28f	+38 (158)	**32e**	+38.5 (156)

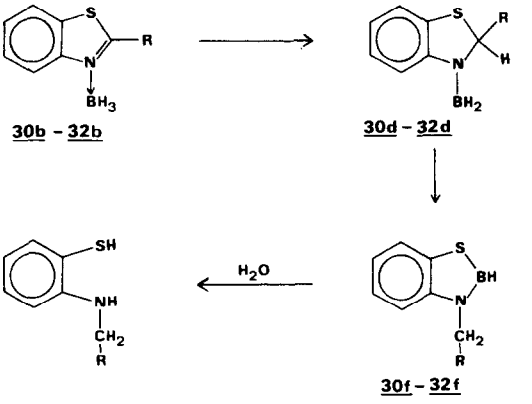
*See footnote, Table 1.

The *N*-borane benzothiazolines **26b–29b** readily transform to heterocycles **26d–29d** and finally to compounds **26f–29f** (Table 7).

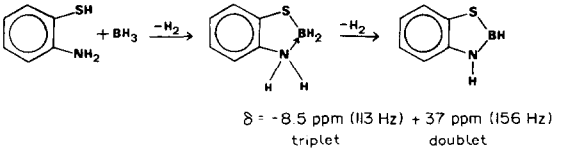


26d R = BH_3
27d - 29d R = electron pair

Similarly *N*-monoborane adducts of benzothiazoles **30b–32b** pass through short lived heterocycles and yield benzothiazoboroles **30f–32f** (Table 7).



Although compounds **30d–32d** were not observed, formation of benzothiazoboroles would presume initial hydroboration of the N=C double bond followed by reductive opening of the S–C bond to give compounds **30e–32e**. The assignment of these structures can be readily done by comparison with the boranes derivatives from aminothiophenols which are reported elsewhere [18].



These results allow us to conclude that stable heterocycle adducts can be formed from diazolidines

when C_2 is a methylene, while substitution promotes opening of the cycle, the exceptions being compounds **8a**, **9a** and **13a**. For sulfur nitrogen heterocycles all the compounds were opened by borane with the exception of compound **22a**. More than one borane equivalent was necessary for opening in most cases.

This procedure allows the synthesis of new borolidine heterocyclic compounds which are difficult to prepare by known methods; moreover, it is remarkable that very crowded diadducts which are suitable species for structural studies were readily obtained.

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