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DIBORANE DERIVATIVES FROM N-ALKYLOXAZABOROLIDINES.

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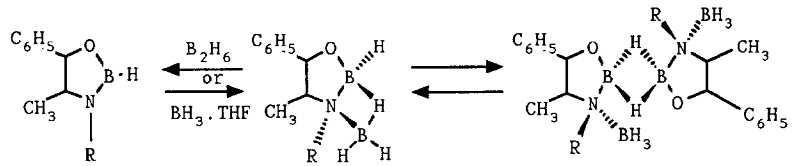
Abstract. N-methyl or N-ethyl oxazaborolidines derived from ephedrines react with B_2H_6 to afford N-BH_3 adducts. N-methyl derivatives dimerize. Monomers and dimers can be considered as diborane derivatives. Borane addition was found to be stereoselective for **8** and **10**.

The high enantioselectivity of oxazaborolidines as reducing agents or catalysts have converted them into valuable reagents[1]. A mechanism has been proposed to explain the high stereoselectivity of the reduction reaction with oxazaborolidines in the presence of BH_3[1a]. We are interested in the study of the nature of this borane complex, in order to add experimental information to the theoretical efforts to explain its behavior[2]. We have already published a new method of preparation of oxazaborolidines[3] from N-acyl derivatives of ephedrines. Herein, we present our results of the investigation into the nature of the borane complexes of these oxazaborolidines.

We have synthesized N-methyl and N-ethyl oxazaborolidines **1-4** derived from ephedrine (*erythro*) and *pseudo*ephedrine (*threo*)[3]. In these heterocycles the oxygen and nitrogen atoms give electronic density to the boron by retrocoordination. It is expected that the donor atoms lose some of their basic properties and the boron atom its acidity. Therefore, it was interesting to explore the coordination ability of these heterocycles.



1 (erythro) R = Et   5 (erythro) R = Et
2 (threo) R = Et   6 (threo) R = Et
3 (erythro) R = Me   7 (erythro) R = Me   9 (erythro) R = Me
4 (threo) R = Me   8 (threo) R = Me   10 (threo) R = Me

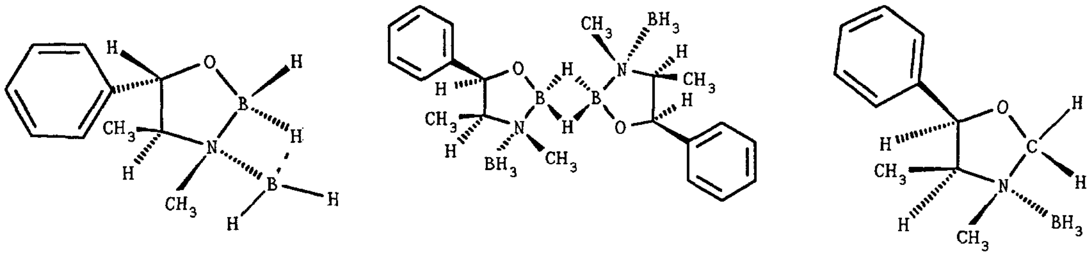
Figure 1.

Adding N-Et_3 to oxazaborolidines **1-4** showed no modification of the corresponding ^{11}B NMR spectra indicating the inert behavior of boron due to a strong retrocoordination bond.

The nitrogen basicity was evaluated by adding B_2H_6 in $CDCl_3$ to **1**, **2** and **4** and B_2H_6 to **3** in a mixture of THF and $CHCl_3$. Compounds **1** and **2** suffered partial conversion to new compounds **5** (12%) and **6** (43%) respectively, as was clearly observed in their ^{11}B NMR spectra. Two new resonances with the same integration appeared for each compound: a doublet near 1 ppm of B-H function and a quartet near -23 ppm for a N-BH_3 adduct, (Table). Both resonances when compared with ^{11}B NMR of compounds **1** and **2** (δ = +28 and +29 ppm respectively[3]) and with N-BH_3 adducts of oxazolidines[4b] (as compound **11** δ= -12.3 ppm, figure 2) appear at abnormally high field. Both changes can be explained by the diborane character of the complexes. As a consequence of the N-BH_3 coordination, the N-B retrocoordination bond is broken and boron acidity is increased, promoting an intramolecular coordination of one hydride to the boron atom. This behavior can also be followed by the ^{13}C NMR because the chemical shifts of **6** are similar to that of the oxazolidine N-BH_3 adducts[4]. Two diastereoisomers were observed for **6** indicating that the nitrogen was converted into a stable chiral atom. Diasteromers for compound **5** could not detected by ^{13}C NMR because of the small concentration of **5** (12%) in the reaction mixture.

Compound **3** reacts with an excess of B_2H_6 in THF and $CDCl_3$, giving traces of compound **7** and adduct **9** (87%). The doublet of the B-H disappears and only a very broad signal is detected at -17.8 ppm. The ^{13}C NMR spectra indicated the presence of only one N-epimer with the N-methyl and C-methyl groups on the same face of the molecule as was deduced from comparison with oxazolidines N-BH_3 adducts derived from ephedrines[4]. The ^{11}B NMR spectrum was interpreted as a result of a fast equilibrium that exchanges the boron atoms in both positions of the dimer structure.

Reaction of compound **4** with B_2H_6 in $CHCl_3$ shows a transformation to compound **8** (60%) and to dimer **10** (20%). ^{13}C NMR showed, again, that only one N-configuration appeared at the nitrogen atom that is shown in figure 2. The nitrogen configuration was clearly evidenced from a nuclear overHauser experiment and from values of the methyl groups displacements, when compared with those of oxazolidine N-BH_3 adducts and boraspiro derivatives[4].



8 **9** **11**[4]

Figure 2

The different behavior detected for N-ethyl and N-methyl oxazaborolidines is attributed to the volume of the ethyl substituent which inhibits dimer formation for compounds **1** and **2**.

Solvent evaporation of the solutions of **5-10** makes the complexes to dissociate to the free oxazaborolidines **1-4** except for **6** which does not completely lose the BH_3, indicating a more stable coordination bond.

Addition of B_2D_6 in $CDCl_3$ to the free oxazaborolidines **1-4** produces the same results as with B_2H_6, but all boron atoms were found to lose their proton coupling indicating fast exchange between them. Triethylamine addition to the BH_3 complexes **5-10** promotes a decrease in the diborane complexes concentration, increasing oxazaborolidine as well as the N-BH_3 adduct of triethylamine ($\delta = -13.0$ ppm). These results confirm the equilibrium between **1-4** and its borane complexes.

N-*tert*butyl-oxazaborolidines failed to give N-BH_3 adducts and N-benzyl give similar results to the N-ethyl derivatives.

Despite the delocalized and planar structure of oxazaborolidine, it is remarkable that they can coordinate to BH_3 giving stable adducts in solution. It is also interesting that N-BH_3 coordination makes acidic the boron in the ring and that a second coordination occurs from a hydride stabilizing the boron atom.

^{13}C and ^{11}B NMR data (δ, ppm; J, Hz)

Compd	C-4	C-4-CH$_3$	C-5	N-R		B-H	N-BH$_3$
5						2.18, d (173)	-22.0, q (93)
6	65.14	13.52	82.30	50.43	10.89	-0.41, d (164)	-23.8, q (95)
	64.64	11.40	83.23	50.97	10.89		
7						6.0, d (173)	-20.8, q (100)
8	69.03	9.82	83.06	44.55		1.47, d (161)	-23.1, q (95)
9	71.90	9.32	80.00	44.40		- 17.8 (br)	
10						- 18.0 (br)	

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