Journal of Organometallic Chemistry, 294 (1985) 1–6
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORON COMPOUNDS

XXVIII *. NOVEL HETEROCYCLIC ORGANOBORANES

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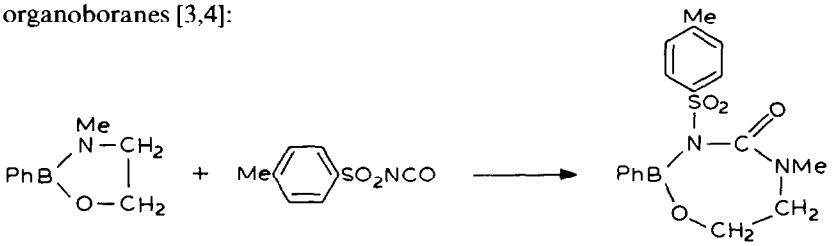
(Received April 1st, 1985)

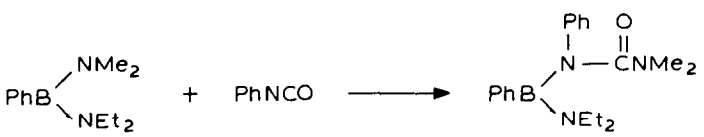
Summary

The preparations of a number of heterocyclic organoboranes, each containing a tertiary nitrogen atom, are reported, and the interactions of these species with organic isocyanates are discussed.

Over the last few years there has been considerable interest in the interaction of aminoboranes and organic isocyanates [2]. Two interesting features of this reaction are (a) where the boron–nitrogen bond is part of a heterocyclic ring the interaction with an organic isocyanate provides a novel synthetic route to large ring organoboranes [3,4]:



and (b) in acyclic aminoboranes the interaction with organic isocyanates results in chain elongation [2]:

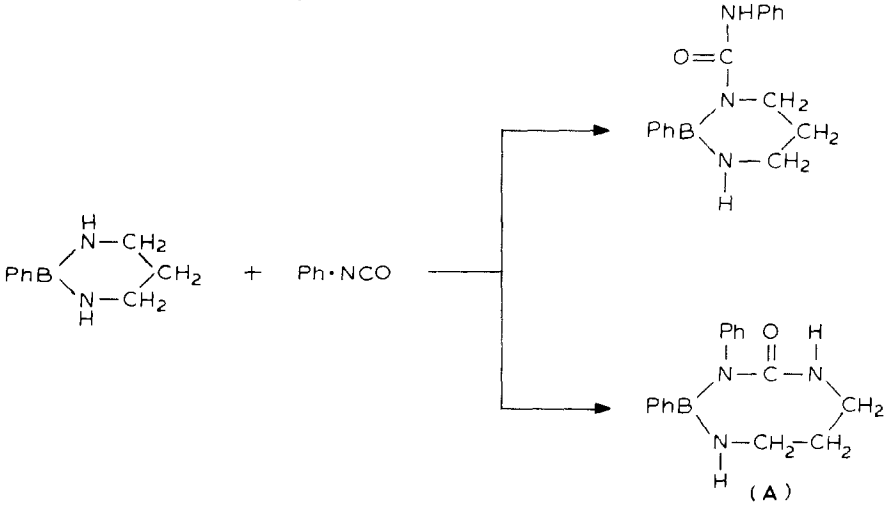


* For part XXVII see ref. 1.

A survey of the literature revealed that although there have been a number of reports concerning the interaction of acyclic aminoboranes with organic isocyanates reports of reactions involving heterocyclic aminoboranes are rather limited.

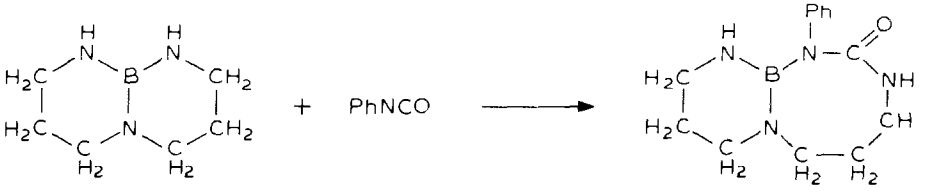
The first report of ring expansion, involving the interaction of phenyl isocyanate and 1,3-di-n-butyl-2-phenyl-1,3,2-diazaboracyclopentane appeared in 1964 [4]. More recently there have been two further publications involving the reaction of phenyl isocyanate with 2-phenyl-1,3,2-diazaboracyclohexane [5,6]. However in systems of this type there are two possible reactions, (a) insertion resulting in ring expansion and (b) an exocyclic reaction.

Gerwarth [6] has formulated (**A**) as the product of the reaction. However in the absence of a crystal structure it is difficult to distinguish between the two possible formulations as they both yield the same product on interaction with an alcohol.



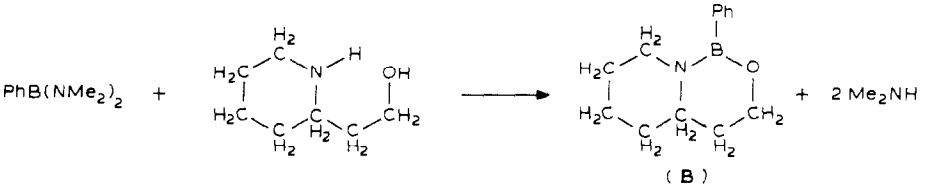
(A)

Fritz [7] has also reported the following reaction but again it is difficult to discount the possibility of an exocyclic reaction:



We have recently prepared a series of heterocyclic organoboranes containing a tertiary nitrogen atom in order to demonstrate that large ring heterocyclic organoboranes can be obtained from the aminoboration of phenyl isocyanate and we now report their synthesis and properties.

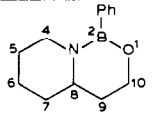
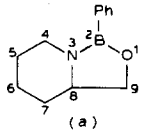
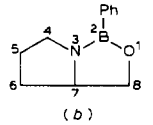
Bis(dimethylamino)phenylborane and 2-piperidine ethanol were refluxed in benzene and afforded, in high yield, 2-phenyl-1,3,2-oxazaborabicyclo[4.4.0]decane (**B**):



(B)

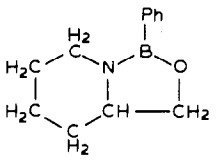
TABLE 1

^{13}C NMR ASSIGNMENTS FOR HETEROCYCLES **B**, **C** AND **D**

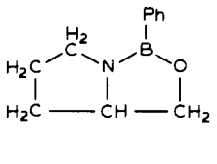
	C(1)	*o*	*m*	*p*	4	5	6	7	8	9	10
	138.33	134.68	128.25	129.47	48.90	28.63	26.88	35.31	54.36	35.31	61.39
 (a)	– –	133.47	127.53	129.35	43.31	26.93	23.90	32.88	59.31	71.7.	
 (b)	131.63 –	134.32	127.65	130.07	43.68	27.90	31.66	64.18	71.47	–	

[a] Recorded in $CDCl_3$. [b] Recorded at −12°C.

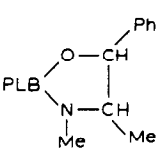
In analagous reactions the heterocycles (**C**, **D**, **E** and **F**) were obtained from the interaction of bis(dimethylamino)phenylborane with 2-piperidine methanol, 2-pyrrolidine methanol, ψ-ephedrine and *N*-methyl anthranilic acid. All compounds were obtained in high yields and purified by distillation under reduced pressures.



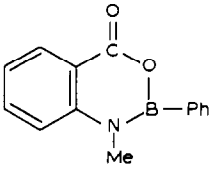
(C)



(D)



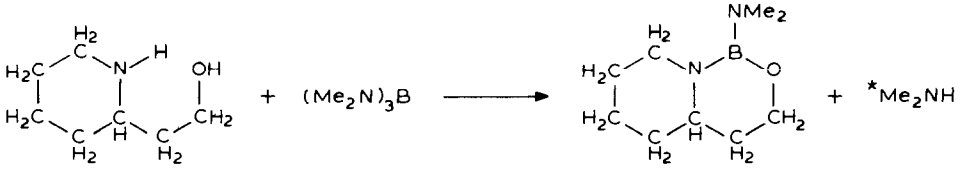
(E)



(F)

Although the ^1H NMR spectra were too complicated for any valuable information to be obtained it was possible to fully analyse the ^{13}C NMR spectra in the case of heterocycles **B**, **C** and **D** (Table 1). By recording the ^{13}C NMR spectra in the absence of a solvent we were able to observe in **B** and **D** the signals for the boron-bonded carbon atom. A previous publication reported that this signal was not observed in the ^{13}C NMR spectrum of **D** [8].

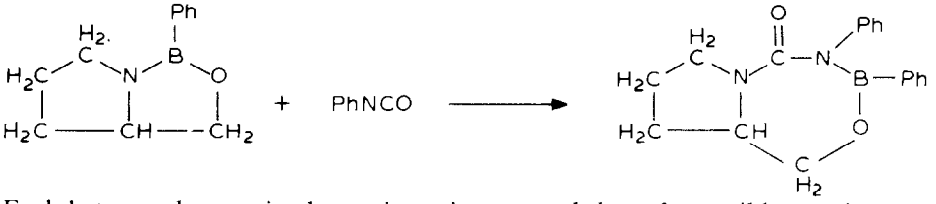
The interaction of tris(dimethylamino)borane and 2-piperidine methanol or 2-piperidine ethanol, in refluxing benzene, resulted in the formation of the corresponding 2-dimethylamino derivatives:



However, we were unable to obtain the corresponding 2-diethylamino derivatives from tris(diethylamino)borane and the amino alcohol even after prolonged refluxing in benzene or higher boiling solvents.

The heterocycles **B**–**F** were treated with phenyl isocyanate or *p*-tolylsulphonyl

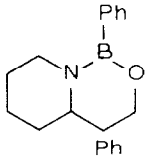
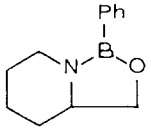
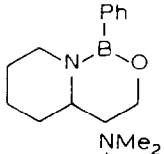
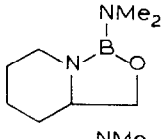
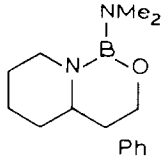
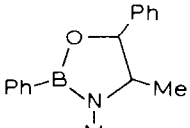
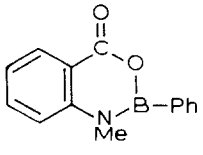
isocyanate and in each case the expected product was obtained, e.g.:



Each heterocycle contained a tertiary nitrogen and the only possible reaction would therefore result in ring expansion.

With the exception of *F*, which was a liquid, the products of the aminoboration of phenyl or *p*-tolylsulphonyl isocyanate were white crystalline compounds. The infrared spectrum of each compound contained a characteristic carbonyl stretching

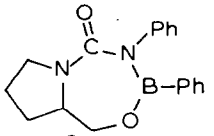
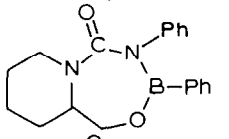
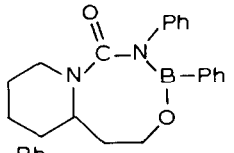
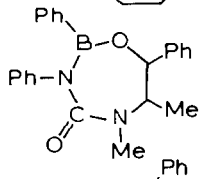
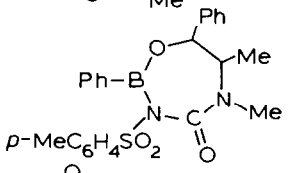
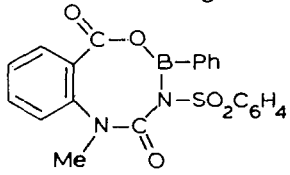
TABLE 2

Compound	Yield (%)	B.p./m.p. (°C) (°C / mmHg)	Found (calcd.) (%) C	H	N
	90	100/0.1	70.2 (70.6)	7.9 (7.5)	7.4 (7.5)
	85	120/0.3	71.1 (71.6)	7.9 (8.0)	6.7 (7.0)
	85	125/0.1	72.5 (72.6)	8.6 (8.4)	6.8 (6.5)
	80	75/0.8	57.2 (57.1)	10.6 (10.1)	16.7 (16.7)
	80	75/0.1	*a*		
	85	125/0.1	77.3 (76.5)	8.1 (7.2)	5.5 (5.6)
	75	160/0.1	70.2 (70.9)	5.6 (5.1)	5.7 (5.9)

[a] Found: 182.158 412. $C_9H_{19}N_2BO$ calcd.: 182.1590362; error 2.17 ppm.

TABLE 3

REACTIONS OF BORON HETEROCYCLES WITH ISOCYANATES

Compound	Yield (%)	B.p./m.p. (°C)	ν(CO)	Found (calcd.) (%) C	H	N
	90	76.7	1665	71.0 (70.6)	5.9 (6.2)	9.7 (9.2)
	90	105	1660	70.4 (71.3)	7.1 (6.6)	8.8 (8.8)
	90	155	1725	72.4 (72.2)	7.0 (6.8)	8.1 (8.3)
	90	90.3	1765	74.3 (74.6)	6.3 (6.2)	7.6 (7.6)
	90	145/0.05	1660	64.6 (64.3)	6.3 (5.6)	5.8 (6.3)
	80	90.2	1770	59.5 (60.8)	4.4 (4.4)	6.1 (6.5)

frequency band. The properties of the heterocycles and their ring expanded compounds are given in Tables 2 and 3.

The success of the aminoboration reaction suggests that the interaction of an organic isocyanate and a heterocyclic organoborane, containing a boron–nitrogen bond, is a convenient method for the synthesis of large ring organoboranes.

Experimental

The ^{13}C NMR spectra were recorded on a JEOL PS100 FT spectrometer; line positions are relative to internal TMS and the compounds were studied as solutions in CCl_4, $CDCl_3$ or as neat samples. Chemical shifts quoted are correct to ± 0.05 ppm. An internal DMSO capillary lock was used when measuring the ^{13}C NMR spectra of neat samples. Bis(dimethylamino)phenylborane [9,10] and tris(dimethyl-

amino)borane [11] were obtained by previously published methods. The usual precautions were taken as is normal for air sensitive starting materials and products.

One example of each type of experiment is reported in detail with the properties of the compounds prepared quoted in Tables 2 and 3.

Preparation of 2-phenyl-1,3,2-oxazaborabicyclo[4.4.0]decane

Bis(dimethylamino)phenylborane (3.52 g, 0.02 mol) was added to 2-piperidineethanol (2.58 g, 0.02 mol) in benzene (50 cm^3). The mixture was refluxed for 5 h and on removal of the solvent the residue on distillation afforded 2-phenyl-1,3,2-oxazaborabicyclo[4.4.0]decane (3.66 g, 85%) b.p. 125°C/0.1 mmHg.

Preparation of 2-dimethylamino-1,3,2-oxaborabicyclo[4.3.0]nonane

Trisdimethylaminoborane (2.86 g, 0.02 mol) and 2-piperidinemethanol (2.30 g, 0.02 mol) were refluxed in benzene (50 cm^3) for 5 h. On removal of the solvent the residue on distillation afforded 2-dimethylamino-1,3,2-oxaborabicyclo[4.3.0]nonane (2.69 g, 80%) b.p. 75°C/0.8 mmHg.

Interaction of phenyl isocyanate and 2,5-diphenyl-3,4-dimethyl-1,3,2-oxazaboracyclopentane

Phenyl isocyanate (1.19 g, 0.01 mol) and 2,5-diphenyl-3,4-dimethyl-1,3,2-oxazaboracyclopentane (2.51 g, 0.01 mol) were dissolved in toluene. The mixture was refluxed for one day and on removal of the solvent the residue, after purification, yielded the ring expanded insertion product (3.33 g, 90%) m.p. 90–93°C.

References

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