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ORGANOBORON COMPOUNDS

XXX *. POLYCYCLIC BORAZINES

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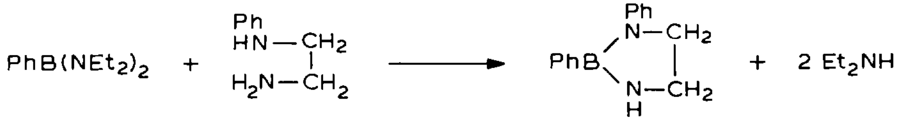
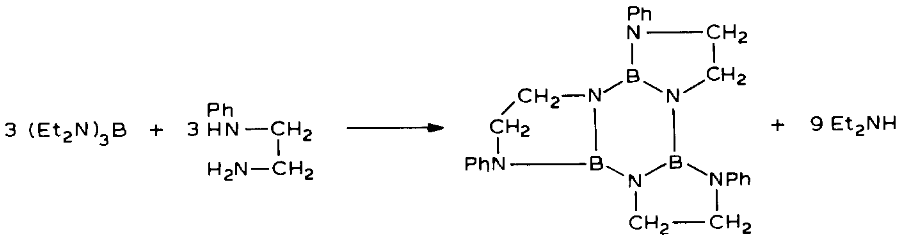
Summary

Polycyclic borazines are readily obtained from the interaction of a tris(dialkylamino)borane with a diamine or amine alcohol. In some cases the 2-dialkylamino-1,3,2-bōracycloalkanes have been isolated.

We have for some time been evaluating the aminoboration reaction as a synthetic route to organoboron heterocycles [2–5]. For example, the interaction of bis(diethylaminophenyl)borane and *N*-phenylethylenediamine gave the corresponding 1,2-diphenyl-1,3,2-diazaboracyclopentane.



In contrast the interaction of tris(diethylamino)borane and *N*-phenylethylenediamine gave a polycyclic borazine, and all attempts to isolate 1-phenyl-2-diethylamino-1,3,2-diazaboracyclopentane were unsuccessful.



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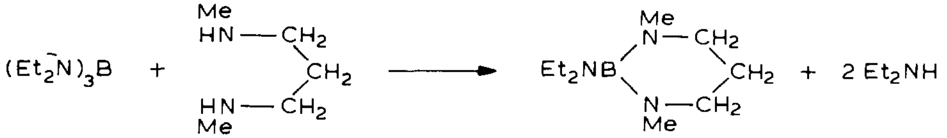
* For part XXIX see ref. 1.

However, the interaction of tris(diethylamino)borane and *N*,*N'*-dimethyl-1,3-propanediamine gave 2-diethylamino-1,3-dimethyl-1,3,2-diazaboracyclohexane.



When this work began there were very few examples of heterocyclic organoboranes in which the exocyclic substituent was a dialkylamino group and one of the ring substituents was an NH group. Reports in the literature have suggested that unless the nitrogen atom in the ring is protected by an organic group compounds of this type tend to undergo intermolecular condensation at relatively low temperatures to give a polycyclic borazine [6,7]. We have now investigated the interaction of a tris(dialkylamino)borane and *N*-alkyl (or phenyl) diamines or amine alcohols and in some cases have been able to isolate the corresponding 2-dialkylamino-substituted heterocycles. In addition to the cases described in our preliminary communication [5] two examples of this type of heterocycle have been reported, namely, the synthesis of 2-diethylamino-1,3,2-thiazaboracycloheptane, which was obtained from the transamination of cysteamine and tris(diethylamino)borane [8], and 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaborocyclopentane, obtained from the interaction of tris(diethylamino)borane and benzamidoxime [4].

In a detailed study of the interaction of tris(dialkylamino)boranes and *N*-alkyldiamines the isolation of 2-dialkylamino-1,3,2-diazaboracycloalkanes was found to depend upon two factors, namely (i) the size of ring formed, and (ii) the type of trisdialkylaminoborane. The importance of these two factors is illustrated by the following observations.

The interaction of tris(dialkylamino)borane and an *N*-alkyl-1,2-diaminoethane gave the polycyclic borazine and attempts to isolate any intermediate were unsuccessful. This observation is in agreement with previously reports [6,7,9]. In contrast the interaction of tris(dimethylamino)borane or trisdiethylaminoborane but not tris(di-n-propylamino)borane and *N*-ethyl-1,3-diaminopropane resulted in the formation of the corresponding 2-dialkylamino-1,3,2-diazaboracyclohexane derivative in addition to the polycyclic borazine.

The analytical data and physical properties of the 2-dialkylamino-1,3,2-diazaboracyclohexanes are given in Table 1. The compounds were mobile liquids and their infrared spectra contained bands in the regions 3400, 1357 ± 33 and 1509 ± 9 cm^{-1} characteristic for $\nu(\text{NH})$, $\nu_{as}(\text{BN})$ and $\nu_s(\text{BN})$, respectively. In the mass spectra the molecular ions were observed.

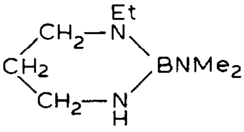
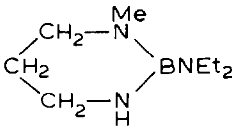
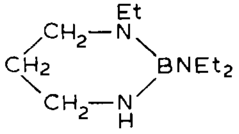
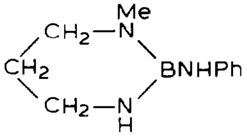
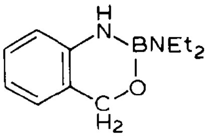
2-Dialkylamino-1,3,2-diazaboracyclohexanes also underwent transamination reactions. A typical reaction was that of 1-methyl-2-diethylamino-1,3,2-diazaboracyclohexane with aniline to give the 2-anilino derivative.

The interaction of tris(dialkylamino)boranes and amine alcohols followed a similar pattern to those with diamines. For example, 2-diethylamino-1,3,2-oxazaboracyclohexane was obtained from tris(diethylamino)borane and 3-amino-1-propanol. In contrast we were only able to isolate the polycylic borazine from the reaction of tris(diethylamino)borane and 2-amino-1-propanol.

There have been a number of reports concerning the preparation of polycyclic

TABLE 1

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR 2-DIALKYLAMINO-1,3,2-DIAZA(OXAZA)-BORACYCLOHEXANES

Compound	Yield (%)	B.p. (°C/ mmHg)	n_D^{25}	Analysis (Found (calcd.)(%))			MW [a]
				C	H	N	
	26	40–46/ 0.2	1.4772 (22)	53.2 (54.1)	10.7 (11.6)	26.3 (27.1)	155
	53	54–60/ 0.5	1.4769	48.6 (50.0)	9.6 (9.3)	28.7 (29.1)	169
	44	60/01	1.4605 (27)	59.2 (59.0)	11.9 (12.0)	22.6 (22.9)	183
	71	46/1.0	1.5651 (21)	61.8 (63.4)	8.1 (8.5)	21.9 (22.2)	189
	37	50–52/ 0.01	1.4588 (23)	53.5 (53.8)	10.7 (10.9)	17.7 (17.9)	156
	43	102–104/ 0.01	–	65.0 (64.7)	8.6 (8.3)	13.3 (13.7)	204

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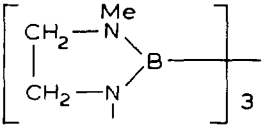
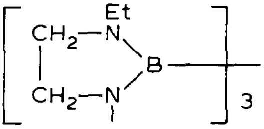
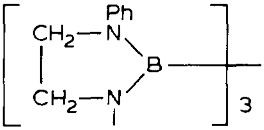
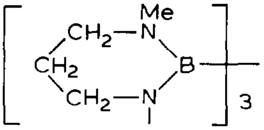
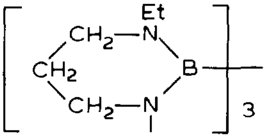
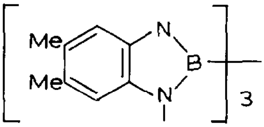
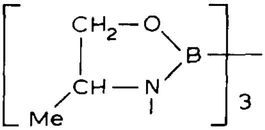
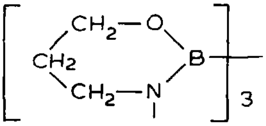
[a] Determined by mass spectrometry.

borazines [10,11]. In all our reactions involving interactions of tris(dialkylamino)boranes and a diamine or amine alcohol the corresponding polycyclic borazine was obtained in a yield which was increased by extended refluxing of the reactants. The physical properties and analytical data of the polycyclic borazines are listed in Table 2. All the polycyclic borazines were purified by sublimation and in the mass spectra the molecular ions were observed. Their infrared spectra contained bands in the regions 1522–1504 and 1495–1490 cm^{-1} characteristic for the γ_{str}(BN) when N and O are bonded to a boron atom in the ring. A characteristic doublet, due to B–N ring deformation, was also observed in the region 714–683 cm^{-1} [12].

The isolation of 2-dialkylamino-1,3,2-diaza(oxaza)boracyclohexanes strongly suggests that the formation of polycyclic borazines in the reaction of tris(dialkyl-

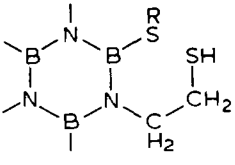
TABLE 2

POLYCYCLIC BORAZINES

Compound	Yield (%)	M.p. (°C)	Analysis (Found (calcd.)(%))			MW [a]
			C	H	N	
	90	155–160	43.6 (43.9)	8.8 (8.5)	33.8 (34.1)	246
	79	43–46	49.4 (50.0)	9.3 (9.4)	27.8 (29.2)	288
	87	207–210	66.2 (66.7)	6.5 (6.3)	19.7 (19.4)	432
	56	135–136	48.6 (50.0)	9.6 (9.4)	27.8 (29.2)	288
	65	123–125	53.9 (54.5)	9.4 (10.0)	24.6 (25.4)	330
	52	~ 300	66.3 (66.6)	6.5 (6.3)	19.35 (19.4)	
	48	143–147	42.11 (43.4)	7.0 (7.2)	15.9 (16.9)	249
	96	110–115	43.04 (43.4)	7.2 (7.2)	17.4 (16.9)	249

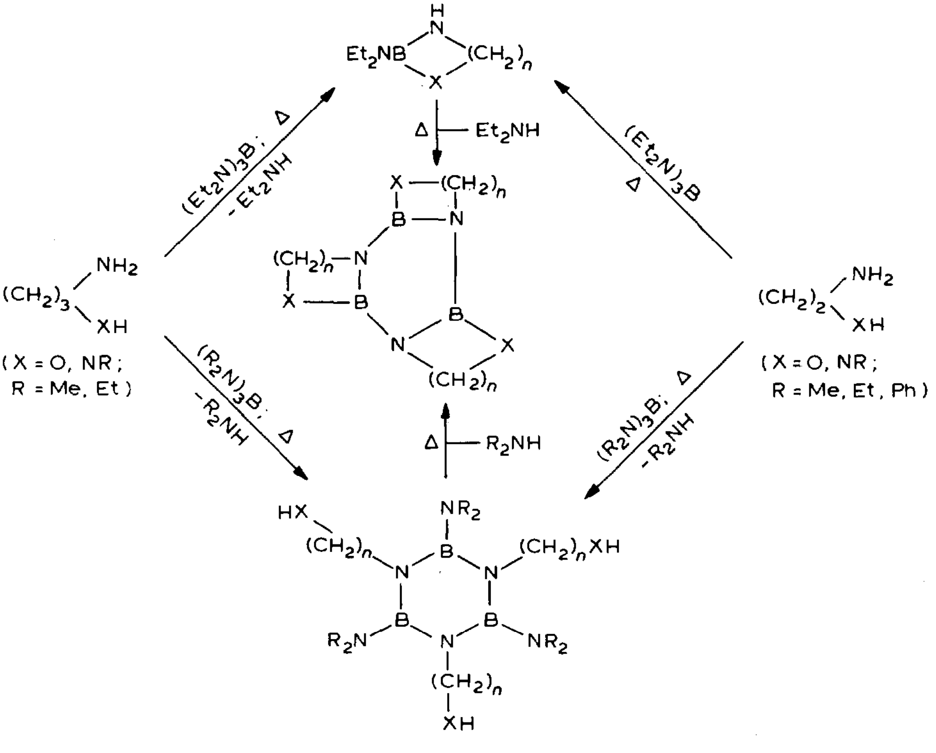
[a] Determined by mass spectrometry.

amino)boranes with diamines or amine alcohols may follow a different mechanism from that operating when tris(alkylthio)boranes are used [8]. All attempts to isolate 2-alkylthio-1,3,2-diazaboracycloalkenes were unsuccessful, and the mass spectrum of an incomplete reaction between a tristhioborane and cysteamine showed the presence of the intermediate A.


(A)

This indicates that formation of the borazine ring is followed by the elimination of mercaptan. Similar observations were made during a study of the interaction of a tristhioborane and 3-amino-1-propanol.

Our results therefore strongly suggest that the formation of polycyclic borazines can proceed by at least two routes (Scheme 1), namely (a) formation of the borazine ring followed by amine elimination, and (b) formation of a heterocyclic intermediate followed by amine elimination and cyclisation.



(n = 2,3)

SCHEME 1

Experimental

Infrared spectra were recorded on a Perkin–Elmer 457 grating spectrometer using potassium bromide optics. The mass spectra were measured on an AEI MS 902 spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced using a cooled direct-insertion probe. The usual precautions, necessary for air-sensitive starting materials and products were taken. Tris(dimethylamino)borane [13], tris(diethylamino)borane [14], tris(di-n-propylamino)borane [15] and bis(diethylamino)phenylborane [16] were prepared by established methods. As the experimental procedure was the same in all cases only typical examples are discussed in detail. Analytical and physical data are given in Tables 1 and 2.

Preparation of 1,2-diphenyl-1,3,2-diazaboracyclopentane

A solution of bis(diethylamino)phenylborane (1.60 g, 0.007 mol) and *N*-phenylethylenediamine (0.94 g, 0.007 mol) in benzene was refluxed for 6 h. The volatiles were removed under reduced pressure and the residue distilled to give 1,2-diphenyl-1,3,2-diazaboracyclopentane (1.05 g, 68.5%) b.p. 146–148°C/0.05 mmHg, m.p. 55.8°C (Found: C, 75.70; H, 7.32; N, 12.63. *M* 222. $C_{14}H_{15}N_2B$ calcd.: C, 75.67; H, 6.75; N, 12.61%. *M* 222).

Preparation of 1,3-dimethyl-2-diethylamino-1,3,2-diazaboracyclohexane

A solution of *N,N'*-dimethyl-propane-1,3-diamine (2.26 g, 0.02 mol) and tris(diethylamino)borane (5.1 g, 0.02 mol) in benzene was refluxed for 5 h. The volatiles were removed under reduced pressure, and the residue distilled to give 1,3-dimethyl-2-diethyl-amino-1,3,2-diazaboracyclohexane (1.96 g, 48.5%), b.p. 52–54°C/0.5 mmHg, n_D^{23} 1.4577, (Found: C, 60.11; H, 12.30; N, 22.46; *M* 183. $C_9H_{22}N_3B$ calcd.: C, 59.01; H, 12.02; N, 22.91%. *M* 183).

Preparation of 2-diethylamino-1,3,2-oxazaboracyclohexane

A solution of 3-amino-1-propanol (1.92 g, 0.02 mol) and tris(diethylamino)borane (5.80 g, 0.02 mol) in benzene was refluxed for 26 h, the solvent was removed under reduced pressure and the residue distilled to give 2-diethylamino-1,3,2-oxazaboracyclohexane (1.50 g, 37%), b.p. 50–52°C/0.01 mmHg, n_D^{23} 1.4588. (Found: C, 53.51; H, 10.7; N, 17.7; *M* 156. $C_7H_{17}BN_2O$ calcd.: C, 53.8; H, 10.9; N, 17.9%. *M* 156).

Preparation of 1-methyl-2-phenylamino-1,3,2-diazaboracyclohexane

A solution of aniline (1.65 g, 0.01 mol) and 1-methyl-2-diethylamino-1,3,2-diazaboracyclohexane (3.0 g, 0.01 mol) in benzene was refluxed for 5 h. The solvent was removed under reduced pressure and the residue distilled to give 1-methyl-2-phenylamino-1,3,2-diazaboracyclohexane (2.4 g, 71.0%), b.p. 46°C/1.0 mmHg, n_D^{21} 1.5651. (Found: C, 61.8; H, 8.1; N, 21.9; *M* 189. $C_{10}H_{16}BN_3$ calcd.: C, 63.4; H, 8.5; N, 22.2%; *M* 189).

Preparation of S-triazatriborino (2,1-b′4,3-b′:6,5-b″) 3,5,7-trimethyl, tris (1,3,2)-diazaboracyclohexane

N-Methyl-1,3-propanediamine (10.12 g, 0.1 mol) was mixed with tris(diethylamino)borane (2.0 g, 0.1 mol) at room temperature, toluene was added, and the mixture refluxed for 16 h. The solvent was removed under reduced pressure and the residue distilled to give 1-methyl-2-diethylamino-1,3,2-diazaboracyclohexane, b.p. 54–60°C/0.5 mmHg leaving a residue which on sublimation (122°C/0.1 mmHg) gave S-triazatriborino (2, 1-*b* 4,3-*b*′ : 6,5-*b*″) 3,5,7-trimethyl, tris (1,3,2)-diazaboracyclohexane (6.21 g, 56%), m.p. 135–136°C. Found: C, 48.6; H, 9.6; N, 27.8; *M* 288. $C_{12}H_{27}B_3N_6$ calcd.: C, 50.0; H, 9.3; N, 29.1%; *M* 288). Refluxing the solution for a longer time led to yields of the borazine of up to 98% without the separation of the intermediate. The same borazine was obtained when tris(di-n-propylamino)borane was treated with *N*-methyl-1,3-propanediamine; no intermediate could be isolated in this reaction.

References

1 Part XXIX. R.H. Cragg, T.J. Miller and D.O'N. Smith, J. Organomet. Chem., 302 (1986) 19.
2 R.H. Cragg and M. Nazery, J. Chem. Soc., Dalton Trans., (1974) 162.
3 R.H. Cragg and A.F. Weston, J. Chem. Soc., Dalton Trans., (1975) 93.
4 R.H. Cragg and T.J. Miller, J. Chem. Soc., Dalton Trans., (1982) 907.
5 R.H. Cragg and M. Nazery, Inorg. Nucl. Chem. Lett., 10 (1974) 481.
6 K. Niedenzu and C.D. Miller, Fort. Chem. Forsh., 15 (1970) 191.
7 K. Niedenzu and P. Fritz, Z. Anorg. Allgem. Chem., 340 (1965) 329.
8 R.H. Cragg and A.F. Weston, J. Chem. Soc., Dalton Trans., (1973) 1054.
9 K. Niedenzu, P.J. Busse and C.D. Miller, Inorg. Chem., 9 (1970) 977.
10 R.H. Cragg and A.F. Weston, J. Chem. Soc., Dalton Trans., (1975) 1761.
11 J.J. Harris and B. Rudner, J. Org. Chem., 27 (1962) 3848.
12 A. Meller, Organomet. Chem. Rev., 2 (1967) 1.
13 D.W. Aubrey, M.F. Lappert and M.K. Majumdar, J. Chem. Soc., (1962) 4088.
14 W. Gerrard, M.F. Lappert and C.A. Pearse, J. Chem. Soc., (1957) 381.
15 D.W. Aubrey, W. Gerrard and E.F. Mooney, J. Chem. Soc., (1962) 1786.
16 K. Niedenzu, H. Beyer and J.W. Dawson, Inorg. Chem., 1 (1962) 738.