Organoboron Compounds. Part X.[1] Polycyclic Borazines

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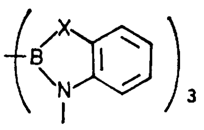
The synthesis of polycyclic borazines, $(BN[CH_2]_nX)_3$ (X = O, NH, or NMe; n = 2 or 3) by reaction of a tris-alkylthioborane with a series of hydroxyamines or diamines is described and their i.r. and mass spectra and possible mechanism of formation are discussed.

POLYCYCLIC borazines of the type (I; X = O, NH, and S) have previously been reported.[2-6] Harris [2] also prepared some phenyl-substituted o-aminophenol borazine derivatives using trimethoxyborane or trihalogenoboranes as the source of boron and also discussed a possible mechanism for the formation of polycyclic borazines. Brotherton [3] reported the preparation of (I; X = O and NH) using trialkoxyboranes, and made reference to the first report of a polycyclic borazine, (I; X = NH).[4] Niedenzu *et al.*[6] prepared (I; X = S) using



(I)

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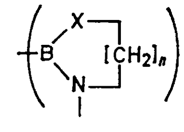
[3] R. J. Brotherton and H. Steinberg, *J. Org. Chem.*, 1961, **26**, 4632.

[4] C. A. Brown, Final Report Office of Naval Research, Contract No. 14939(02) Project No., NR 052-355, September 1956.

[5] H. Beyer, K. Niedenzu, and J. W. Dawson, *J. Org. Chem.*, 1962, **27**, 4701.

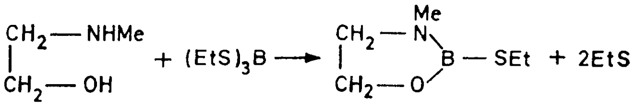
[6] K. Niedenzu, J. W. Dawson, P. W. Fritz, and W. Weber, *Chem. Ber.*, 1967, **100**, 1898.

trichloroborane or bisdimethylaminoborane as the source of boron and also commented on alternative synthetic methods. The polycyclic borazine (II; X = NH and $n = 3$) has been reported[7] and an attempt to prepare (II; X = NH and $n = 2$) gave a mixture of products which could not be separated.[8]

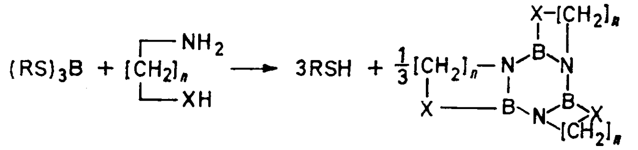


(II)

Thioboranes react readily with alcohols[9] and amines[10] to give the corresponding alkoxy- and amino-boranes. With difunctional organic compounds such as mercapto-alcohols and secondary aminoalcohols the corresponding organoboron heterocycle is obtained [equation (1)].[11] We find, however, that if one of the functional groups is a primary amino-group the product of the reaction is not the expected heterocycle but a polycyclic borazine.



(1)



(2)

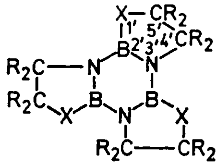
Using this method we have synthesised, in high yields, a series of polycyclic borazines, (II; X = O, NH, and NMe, $n = 2$ and 3). The borazine (II; X = S and $n = 2$) and 1,2:3,4-bisethylenethio-5,6-ethyleneiminoborazine have previously been reported.[12,13]

RESULTS AND DISCUSSION

The general reaction for formation of these polycyclic borazines was that of a trisalkylthioborane with the corresponding substituted amine [equation (2)]. The analytical data and physical constants of 11 polycyclic borazines, prepared by this method, are given in Table 1. The m.p.s tend to be substantially higher than for normal borazines. For example compound (II; X = NH, $n = 3$) has a m.p. of 154—155 °C in contrast to $(MeNHBNMe)_3$[14] which is a liquid and $(Me_2NBNMe)_3$[15] with a m.p. of 64 °C. The m.p. for (II; X = NH, $n = 3$) is in good agreement with that previously reported[7,8] though the yield was considerably improved. Compound (II; X = NH, $n = 2$) is formulated as a trimer because its mass spectrum showed no significant peaks at higher mass numbers than the trimer parent peak; also previous formulation as a polymer[7,8] did not account for the strong NH stretching band at 3 440 cm^{-1} which would not be present if the compound were a polymer.

I.r. Spectra.—The i.r. spectral assignments of the polycyclic borazines, as a group, are compared with those for similar substituted borazines in Table 2.[16] The comparison shows that the two groups exhibit similar bond-stretching frequencies. Substitution of O or NR for X (R = H or Me) in the exocyclic ring of the polycyclic borazines had little effect on the borazine ring B–N frequency, though its position was a little higher when R = H than Me. Exocyclic ring expansion lowered the B–N frequency for the O-substituted compounds but had no effect on the NR compounds; when X = O, methyl substitution at $C^{5'}$ increased the wavelength of ν(BN) and ν(BO) whilst phenyl substitution reduced it. Substitution of Me at $C^{4'}$ had no effect on ν(BN) or ν(BO) but dimethyl substitution lowered the band. Methyl substitution at positions 1′, 4′, or 5′ had no effect when X = NR.

^{11}B *N.M.R. Spectra.*—The ^{11}B n.m.r. spectra of some of the polycyclic borazines were recorded. The compounds $(BNCH_2CHPhO)_3$ and (II; X = NH, $n = 2$) were too insoluble for their spectra to be recorded. Interchange of O and NH as the exocyclic substituent had no effect on the recorded shift (Table 1). Methyl substitution in place of hydrogen at $C^{4'}$ and $C^{5'}$ (X = O) had a greater effect than ring expansion and dimethyl substitution produced an even larger downfield shift. Compound (II; X = S, $n = 2$) showed a much larger downfield shift than when X = O or NH.



X = O or NR
R = H or Me

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TABLE 1

Analytical and spectroscopic data for the borazines $(BN[CH_2]_nX)_3$, (II)

				Analyses/%						Principle ions in the mass spectra[b]					
				Found			Calc.								
Compound	Yield %	M.p. (θ_c/°C)	^{11}B N.m.r. shift[a]	C	H	N	C	H	N	Parent	P − 1	P − 15	P − one exo-cycle	P − two exo-cycles	Base
(II; X = O, n = 2)	82	150		33.8	5.95	19.45	34.8	5.80	20.3	207 (23.4)	206 (59.3)		163 (2.6)	119 (1.6)	P − 1
(II; X = O, n = 3)	74	172	−24	42.15	7.40	16.45	43.35	7.25	16.85	249 (24.4)	248 (53.1)		191 (1.3)	133 (0.8)	P − 1
$(BNCH_2CHMeO)_3$	82	128	−27.5	41.05	6.35	13.65	43.35	7.25	16.85	249 (25.3)	248 (24.5)	234 (26.5)	191 (0.9)	133 (0.2)	P − 15
$(BNCH_2CHPhO)_3$	85	120		63.35	6.40	8.40	66.2	5.50	9.65	435 (28.8)	434 (9.2)		315	195	91 (C_7H_7) 40.2
$(BNCHMeCH_2O)_3$[c]	82	102	−27.5	43.35	7.10	16.55	43.35	7.25	16.85	249 (6.1)	248 (2.6)	234 (71.4)	191 (1.1)	133 (0.4)	P − 15
$(BNCMe_2CH_2O)_3$	91	191	−28.5	49.5	9.25	14.3	49.5	8.25	14.45	291 (0.7)	290 (0.5)	276 (66.7)	219 (1.6)	147 (0.6)	P − 15
(II; X = NH, n = 2)	96	250		33.1	12.5	34.5	35.3	7.35	41.2	204 (17.2)	203 (30.6)		161 (1.2)	118 (0.2)	P − 1
(II; X = NH, n = 3)	94	150	−24	43.45	8.95	33.4	43.9	8.45	34.15	246 (27.9)	245 (29.2)	231 (9.7)	189 (1.8)	132 (0.5)	P − 1
$(BNCHMeCH_2$-$NH)_3$[d]	77	125		39.5	10.75	26.9	43.9	8.55	34.15	246 (12.5)	245 (2.2)	231 (55.5)	189 (1.4)	132 (0.3)	P − 15
(II; X = NMe, n = 2)	69	155—156		43.6	8.30	33.5	43.9	8.55	34.15	246 (20.8)	245 (29.8)	231	189 (1.1)	132 (0.2)	P − 1
(II; X = NMe, n = 3)	88	146—147		49.75	9.65	28.75	50.0	9.35	29.15	288 (27.0)	287 (5.0)	273 (20.9)	217 (1.5)	146 (4.2)	P
(II; X = S, n = 2)			−37.5							255 (17.0)	254 (11.9)		195 (1.3)	135 (0.3)	P

[a] In p.p.m. with respect to $Et_2O{\cdot}BF_3$. [b] Relative intensities as a percentage of the total ionisation are given in parentheses after the *m/e* values. [c] Prepared from L-2-aminopropan-1-ol. [d] The Me group can be attached to either carbon atom.

Mass Spectra.—The mass spectra of all the compounds except (II; X = S, n = 2) (Table 1) showed that in general the major fragmentation route was identical.

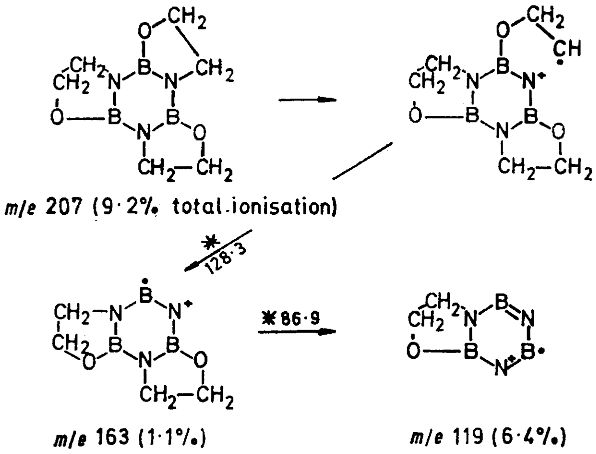
TABLE 2

I.r. assignments for polycyclic borazines

Assignment	Band (cm^{-1})
N–H	3 445—3 440
B–N	1 520—1 470
B–O	1 310—1 230
B–N (cyclic)	1 375—1 347
B–N W_{10} ring def.	956—900
B–N ring out of plane	720—670

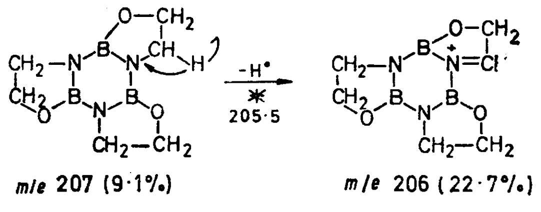
For example in (II; X = O, n = 2) the major fragmentation was *via* loss of exocyclic groups which were accompanied by the corresponding metastables [equation (3)]. The other major fragmentation, (4), was from P^+ to $(P - 1)^+$. Apart from the main fragmentation there were no other peaks in the spectrum of greater than 5% of the base peak. The base peak was the $(P - H)^+$ ion. A strong doubly charged ion, $(P - 2H)^{2+}$, and minor losses of oxygen and H_2O from the parent were observed.

Minor losses of NH_2 and NCH_2 were observed in the spectrum of (II; X = NH, n = 2), the base peak resulting from loss of hydrogen, and a strong $(P - 2H)^{2+}$ ion was also observed. Inclusion of a third CH_2 unit in each exocyclic ring had little effect on the observed fragmentation, although the $(P - H)^+$ peak in (II; X = NH, n = 3) was reduced when compared with that when n = 2. Substitution of a Me group for one of the exocyclic ring-carbon hydrogen atoms in each ring reduced the parent and $(P - H)^+$ ion abundances and the $(P - CH_3)^+$ peak became the base.



(3)

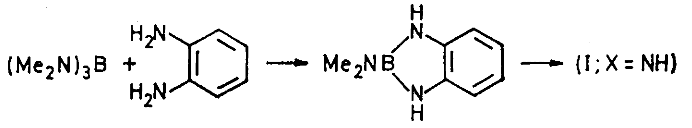
With one exception, the main fragmentation route was *via* successive loss of two exocyclic rings. The compound



(4)

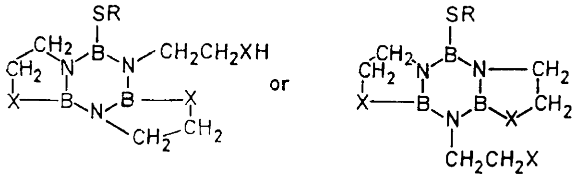
$(BNCH_2CHPhO)_3$, the single exception, fragmented to form ions of the exocyclic rings. Hydrogen loss from the exocyclic ring-carbon atoms occurred from either of the ring carbons (either of the carbon atoms adjacent to a heteroatom in the six-membered rings), although when an oxygen atom was bonded to boron in the exocyclic ring the proportion caused by β cleavage with respect to oxygen was small. Substitution of exocyclic rings stabilised the borazine nucleus by localising primary fragmentation in the exocyclic rings. The borazine nucleus remained intact even after complete loss of two such rings.

Mechanism.—The mechanism by which polycyclic borazines of type (I) are formed has been investigated at some length[2] and it was concluded that the most likely route involved borazine formation followed by exocyclic ring closure. However when trisdimethylaminoborane and *o*-aminoaniline were heated under reflux in diethyl ether for 15 h the monosubstituted product (III) was obtained[5] which was then converted into the borazine on 30 min reflux in xylene [equation (5)]. In all our reactions we were unable to isolate the alkylthioborane corresponding to (III) and obtained the polycyclic borazine. The mass spectra of the products of incomplete reactions showed peaks above the parent for the polycyclic borazine corresponded to the molecular weights of the non-cyclised product containing the borazine ring. Thus trisalkylthioboranes and trichloroborane react to form polycyclic borazines by borazine-nucleus formation as the first step, whilst trisdialkylaminoboranes react in some cases to form a borolan intermediate.

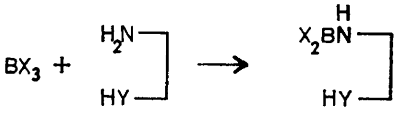


(5)

(III)



Without a detailed study of the reaction mixture during reaction it is difficult to predict the mechanism for formation of a polycyclic borazine. It would appear that in some cases the reaction proceeds *via* B–H borazine formation and in other cases *via* monomer formation. Thus the reaction must be finely balanced between whether a second N hydrogen or that on Y is lost. This will depend on the reactivity of the group attached to boron. Where the group is highly reactive it will react with another group to give borazine formation, whilst where it is less reactive the boron already attached will react again in the group to form a cyclic product, which can in some cases be isolated, and on further reaction give the polycyclic borazine.



EXPERIMENTAL

General Procedure.—I.r. spectra were measured on a Perkin-Elmer 457 grating spectrometer using potassium bromide optics. ^{11}B N.m.r. spectra were recorded on saturated solutions of the compounds in benzene using $Et_2O{\cdot}BF_3$ as external standard using a Perkin-Elmer R10 spectrometer. The mass spectra were measured on an A.E.I. MS 902 spectrometer at 70 eV.* The source was maintained at 170 °C and the compounds introduced as solids using a cooled direct-insertion probe. In general only those peaks of relative intensity greater than 5% were considered.

The usual precautions, necessary for air-sensitive starting materials and product, were taken. Trisethylthio- and tris-n-propylthio-boranes were prepared by established methods.[17] As the experimental procedure was the same in all cases only two examples are discussed in detail and all analytical and physical data for the polycyclic borazines are given in Table 1.

1,2:3,4:5,6-*Trisethyleneoxyborazine.*— Tris-n-propylthioborane (1.73 g, 0.28 mol) and 2-aminoethanol (6.85 g, 0.029 mol) were heated under reflux in benzene for 3 h. On removal of the solvent, a residue was obtained which on sublimation (100 °C, 0.5 mmHg) yielded 1,2:3,4:5,6-*tris-ethyleneoxyborazine* (1.84 g, 92%), m.p. 150 °C (Found: C, 33.8; H, 5.95; N, 19.45%; *M* 207. $C_6H_{12}B_3O_3$ requires C, 34.8; H, 5.8; N, 20.3%; *M* 207).

1,2:3,4:5,6-*Tris*-N-*methylethyleneiminoborazine.*— Trisethylthioborane (4.72 g, 0.023 mol) and *N*-methylethylenediamine (1.77 g, 0.024 mol) were heated under reflux in benzene for 3 h. On removal of the solvent the residue on sublimation (105 °C, 0.3 mmHg) yielded 1,2:3,4:5,6-*tris*-N-*methylethyleneiminoborazine* (1.38 g, 69%), m.p. 155—156 °C (Found: C, 43.6; H, 8.30; N, 33.5%; *M* 246. $C_9H_{21}B_3N_6$ requires C, 43.9; H, 8.55; N, 34.15%; *M* 246).

[4/2301 *Received, 6th November,* 1974]

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* 1 eV ≈ 1.60 × 10^{-19} J, 1 mmHg ≈ 13.6 × 9.8 Pa.

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