

## Special Review

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### MECHANISM OF FORMATION OF APPLICABLE LINEAR BORON-NITROGEN POLYMERS

#### PART I. LITERATURE REVIEW

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This paper contains a literature review on the mechanism of formation of applicable linear boron-nitrogen polymers.

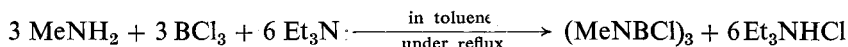
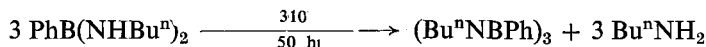
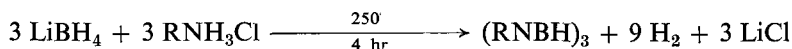
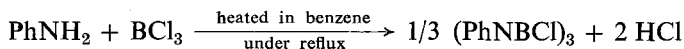
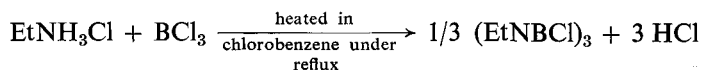
The possibilities of technical development of new boron chemistry were envisaged a little more than 20 years ago, and there was a free flow of sponsorship, particularly from the United States Government Departments, for research began into procedures for producing thermally and chemically stable polymers containing boron as an essential element. The skeletons usually tried have involved B-O-B, B-N-B, B-C-C-B and B-O-M linkages, where *M* is an element such as P, Ti, Al or Si, and combinations of these basic forms can be formulated. The B-B linkage is weak, and may for the present be disregarded.

In connection with the attempts to produce boron polymers, the linear systems appear to offer a potentially good possibility for specific investigation. In the boron-nitrogen system there is a propensity to form trimeric cyclic structures. The nature of the groups attached to the boron or nitrogen in this system affects the hydrolyte stability, and certain factors relating to this have been revealed. In this article an attempt will be made to rationalize the subject of tracing, to make certain generalizations, to classify the reactions which lead to macromolecules.

Polyborazynes, (XB<sub>n</sub>N<sub>n</sub>)<sub>n</sub>, exist as cyclic dimers, trimers and tetramers and linear polymers. The great difficulty in the preparation of linear polyborazines is the overwhelming propensity of the polyborazynes to exist as small rings.

#### Preparation of polyborazines

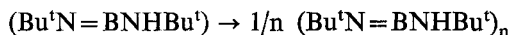
Of the polyborazines, the cyclic trimers, i.e. the borazines, are the best known and in the majority of systems are the usual products in reactions leading to the formation of polyborazynes. The chemistry of the borazines has been well reviewed [1-6]. The following examples illustrate some of the methods available for the preparation of borazines.



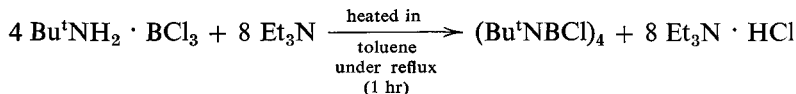
Variation in the substituents on the nitrogen or boron sometimes gives rise to the formation of cyclic dimers and tetramers. Thus, Lappert and Majumdar [7-9] synthesized the cyclic dimer 1,3-di-*tert*-butyl-2,4-*tert*-butylamino-1,3-diaza-2,4-boretane by the pyrolysis of either tris-*tert*-butylamino-borane or bis(di-*tert*-butylamine-boryl)-*tert*-butylamine.

A three-step process was postulated to account for the mechanism leading to the formation of the polyborazine.

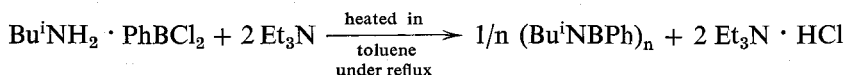
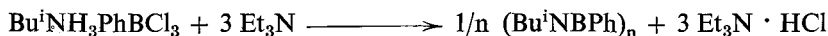
- (1) Intermolecular condensation with the formation of a compound having a B-N-B skeleton:
- (2) Intramolecular 1,3-nucleophilic rearrangement:
- (3) Polymerization of the borazyne:

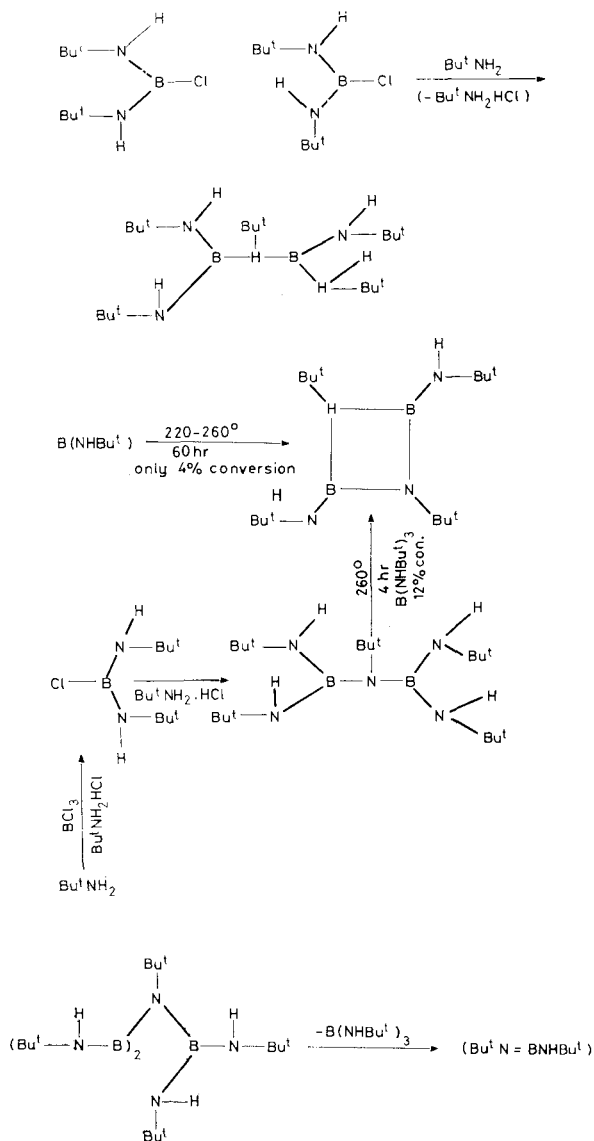


Cyclic tetramers have been prepared by Turner and Warne [10] and Currell *et al.* [11]. Turner and Warne prepared B-tetrachloro-N-tetra-*tert*-butyl borazocine by the pyrolysis of the *tert*-butylamine - boron trichloride 1 : 1 complex in triethylamine:



Currell *et al.* prepared B-tetraphenyl-N-tetra-isobutyl borazocine by dehydrohalogenation of isobutylammonium trichlorophenylborate and isobutylamine - phenylboron dichloride:

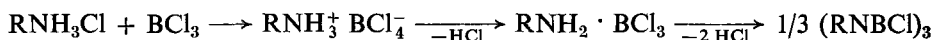
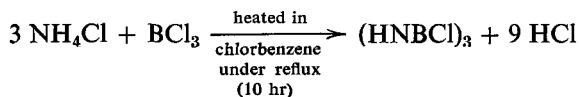




### Reaction paths leading to the formation of polyborazines

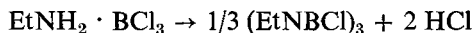
Brown and Laubengayer [12] reported the formation of B-trichloroborazine by heating mixtures of ammonium halide and boron trichloride in an inert medium such as benzene or halobenzene. Butcher and Gerrard [13] further investigated these reactions and showed that there is prior formation of the tetrahaloborate.

On heating, this is followed by the formation of the 1 : 1 complex, ill-defined further intermediates and then the borazine, depending on the b.p. of the solvent used:

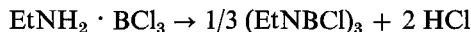


Ill-defined intermediates of the general formula  $(\text{RNHBX}_2)_n \cdot \text{RNH}_3^+ \text{X}^-$  were indicated between the 1 : 1 complex and the borazine. In the isopropyl system the formation of isopropylaminoboron dichloride was also indicated.

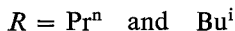
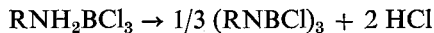
These systems were investigated [14] by thermoanalytical techniques. Thermogravimetric analysis of alkylammonium tetrachloroborates, coupled with pyrolysis studies using bench techniques, indicated intermediates equivalent to the loss of one and three mols of hydrogen chloride, i.e. equivalent to the formation of the 1 : 1 complex and the borazine. No intermediates between the 1 : 1 complex and the borazine were resolved:



Thermogravimetric analysis of the 1 : 1 complexes showed one intermediate equivalent to the loss of two mols of hydrogen chloride, i.e. formation of the borazine:



An examination by bench techniques [15] indicated that pyrolysis of alkylammonium trichlorophenylborate,  $\text{RNH}_3^+ \text{PhBCl}_3^-$ , occurs with the formation of a 1 : 1 complex by loss of HCl or  $\text{C}_6\text{H}_6$ . Further decomposition of trichlorophenylborate systems leads to the formation of the B-trichloro-N-trialkylborazines, the decomposition appearing to involve two concurrent reaction path:



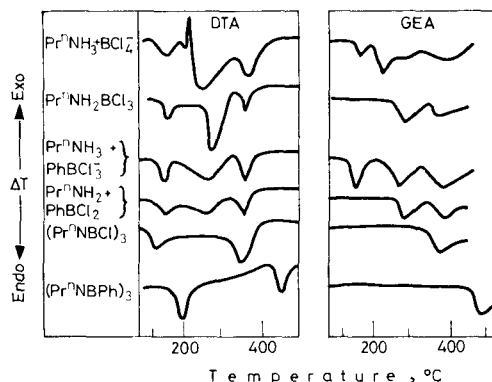
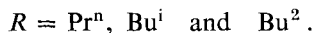


Fig. 1. DTA and GEA curves of the *n*-propyl derivatives

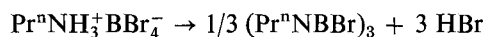
This reaction sequence was further supported by the DTA traces: a comparative study [16] of each trichlorophenylborate,  $\text{Pr}^n\text{NH}_3^+\text{PhBCl}_3^-$ , both 1 : 1 complexes ( $\text{Pr}^n\text{NH}_2^+\text{BCl}_3^-$  and  $\text{Pr}^n\text{NH}_2^+\text{PhBCl}_2^-$ ) and the corresponding B-trichloro-N-tri-*n*-propylborazine 1/3 ( $\text{PhBNPr}^n$ )<sub>3</sub> and B-triphenyl-N-tri-*n*-propylborazine 1/3 ( $\text{PhBNPr}^n$ )<sub>3</sub> is consistent with the above reaction scheme, clearly showing that the trichlorophenylborate and both 1 : 1 complexes all give the B-trichloroborazine with no indication of formation of the B-triphenyl-N-trialkylborazine. The results for the *n*-propyl system are reproduced in Fig. 1.

Decomposition of the tetraphenylborates,  $\text{RNH}_3^+\text{BPh}_4^-$  [15], however, gives the formation of the alkylamine triphenylborane,  $\text{RNH}_2\text{BPh}_3$ , with the evolution of benzene. On further pyrolysis, more benzene is eliminated with the formation of alkylamine diphenylborane:

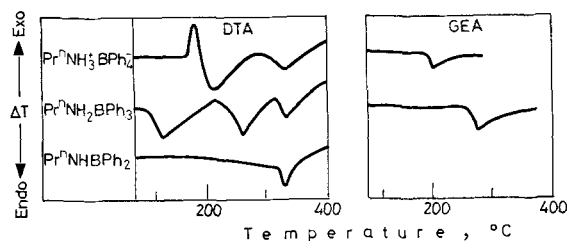
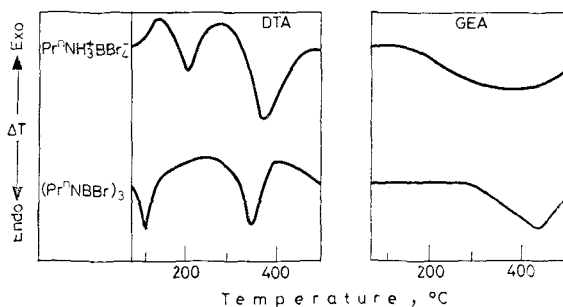


Comparison of the DTA traces of each tetraphenylborate, 1 : 1 complex ( $\text{RNH}_2\text{BPh}_3$ ) and alkylamine diphenylborane ( $\text{RNHBPh}_2$ ) supports the above reaction sequence. The results on the *n*-propyl system are reproduced in Fig. 2.

Pyrolysis of propylammonium tetrabromoborate,  $\text{Pr}^n\text{NH}_3^+\text{BBr}_4^-$ , [16] and application [17] of DTA and GEA leads to results consistent with the reaction sequence



DTA results for *n*-propylammonium tetrabromoborates are reproduced in Fig. 3. A comparison of the curves of the tetrabromoborate and B-tribromo-N-tri-*n*-

Fig. 2. DTA and GEA curves of the *n*-propyl systemFig. 3. DTA and GEA curves of the *n*-propylammonium tetrabromoborates

propylborazine,  $1/3 (\text{Pr}^p\text{NBBR})_3$ , is consistent with formation of the borazine on decomposition of the tetrabromoborate.

The first borazine to be prepared [18] was B-trichloro-N-triphenylborazine, obtained by the thermal decomposition of aniline trichloroborane. The overall reaction suggested in [1] was

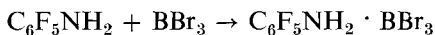


Later workers [2] confirmed that the initial precursor was the aniline – boron trichloride complex, but there was no firm indication of the reaction path between the 1 : 1 complex and the borazine.

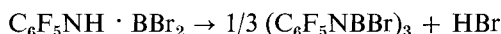
Recent work [19] has shown that arylammonium tetrachloroborates are not easily formed, and when formed are very unstable. A thermoanalytical study [19] of the thermal decomposition of the anilinoboron trichloride 1 : 1 complex has not given any resolution of the intermediates between the 1 : 1 complex and B-trichloro-N-triphenylborazine.

Turner and co-workers [20] studied the kinetics of the decomposition of the aniline – boron trichloride 1 : 1 complex when heated in toluene under reflux (the adduct was soluble in this medium), and showed that the evolution of the first mol of hydrogen chloride followed first-order kinetics, but that the evolution of the second mol of hydrogen chloride followed progressively second-order

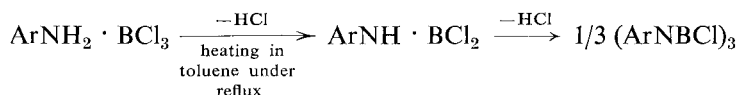
kinetics. Nayer and Peacock [21] examined the decomposition of the pentafluoroaniline – borontribromide complex and were able to isolate the pentafluoroanilinoboron dibromide on heating at 50°:



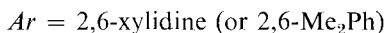
Further heating of the pentafluoroanilinoboron dibromide at 70° in benzene gave B-tribromo-N-tripentafluoroanilinoborazine:



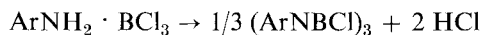
Examination of the thermal decomposition of orthosubstituted arylamine – boron trichloride complexes by Turner and co-workers [20] has shown that if the heating of the *o*-toluidine – boron trichloride complex is stopped after one mol of hydrogen chloride has been lost the borazene ( $\text{ArNH} \cdot \text{BCl}_2$ ) is obtained, from which the borazine ( $\text{ArNBCl}$ )<sub>3</sub> results on loss of a further mol of hydrogen chloride:



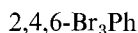
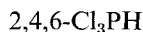
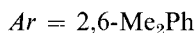
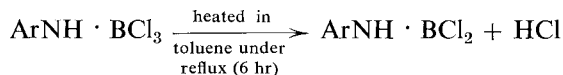
Turner *et al.* [20] also investigated the thermal decomposition of the 1 : 1 complexes of 2,6-disubstituted anilines and boron trichloride. These readily lose 1 mol of hydrogen chloride on heating in toluene under reflux for 3 min, with formation of the borazenes, but thereafter the reaction is slow and the B-trichloroborazine is not formed:



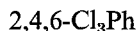
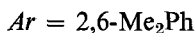
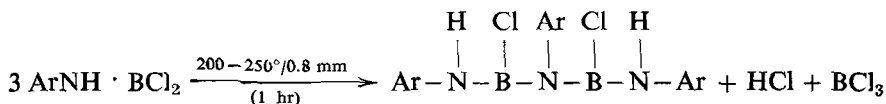
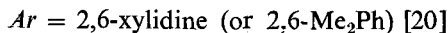
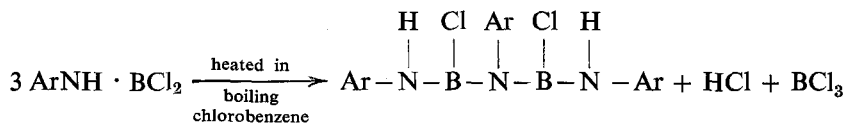
Currell and Beck [19] have obtained similar results. Thus, where there is a single substituent in the ortho position the borazine is obtained on heating in toluene under reflux:



For the di-ortho-substituted anilines the dehydrohalogenation stops at the borazene stage:

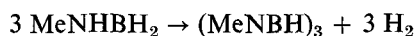
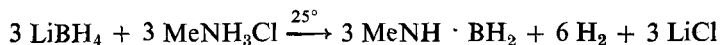


Turner *et al.* [20] and Currel *et al.* [19] have shown that if these borazenes are heated they decompose with loss of hydrogen chloride and boron trichloride to give linear boronamine:

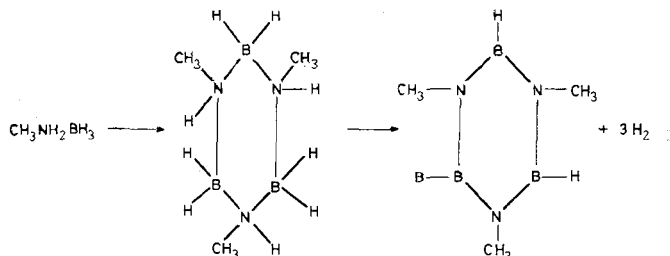


In section (2) there has been given the example of the formation of N-triethylborazine by the interaction of lithium tetrahydroborate with ethylammonium chloride.

Schaeffer *et al.* [4] showed that the initial step was the formation of the 1 : 1 complex:



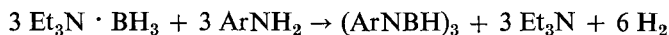
On heating of methylamine borane [21, 22] in monoglyme under reflux for 5 hr, the borazene ( $\text{H}_2\text{BN}(\text{CH}_3)\text{H}$ )<sub>3</sub> is obtained and may be isolate. On heating at 200° for 4.5 hr, the polyborazene ( $\text{CH}_3\text{NBH}$ )<sub>3</sub> is obtained.



Currell and Atkinson [23] prepared B-triarylborazine by using the interaction of triethylamine borane and the aromatic amine, heated together in the absence

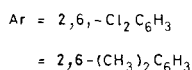
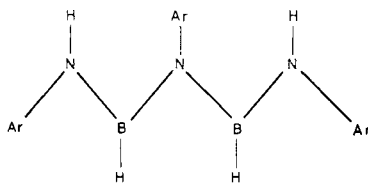


of a solvent at 140–180°:



(e.g. *Ar* = phenyl and *o*-chlorophenyl)

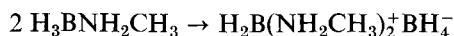
When the reaction was carried out using 2,6-dichloro-aniline, a boronamine was obtained:



When these boronamines were heated at 180–190° with triethylamine borane in excess, the borazine was obtained:



Beachley [25] suggested the following scheme for the formation of 1,3,5-trimethylcycloborazane by the pyrolysis of methylamine borane at 110°:



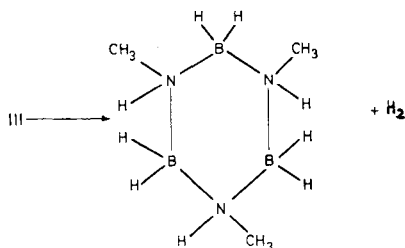
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II

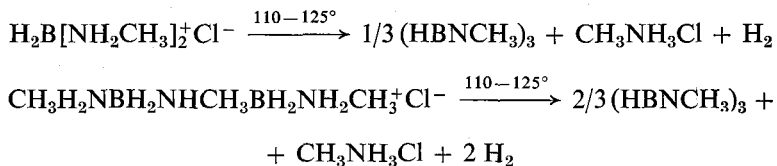


III



(i.e. the boron-nitrogen units are joined together in the formation of the borazene).

Beachley [26] has further studied possible intermediates in the formation of 1,3,5-trimethylborazine by the reaction scheme given below:



He suggests that the compound



is the primary intermediate in the formation of the borazine ring; a molecule of  $\text{CH}_3\text{NH}_2$  is then eliminated, which acts as a base to remove a proton, to give species such as



or



This could ring-close by intramolecular dehydrogenation between the two ends of the chain, giving cyclohexene analogues, which would then lose the second and third molecules of hydrogen to give the borazine.

Beachley [26] studied the pyrolysis of  $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+\text{Cl}^-$  at  $110^\circ$  in a mass spectrometer, and reported the possible formation of  $(\text{H}_2\text{BNHCH}_3)_3$ . However, on heating of the compound  $(\text{H}_2\text{BNHCH}_3)_3$  at  $110^\circ$  for 11 days, only 14% was decomposed: therefore,  $(\text{H}_2\text{BNHCH}_3)_3$  is probably not an intermediate in the borazine formation. There is the possibility of catalysis of the decomposition of the cyclotriborazane; the ammonium ion has previously been observed to be a catalyst for the dehydrogenation of amine borane  $\text{BNH}_2\text{BH}_3$ . The pyrolysis of a mixture of  $(\text{H}_2\text{BNHCH}_3)_3$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  at  $110^\circ$  for 24 hr gave 63% of the possible borazine. The catalyst  $\text{CH}_3\text{NH}_3\text{Cl}$  might provide a low-energy path for the formation of



Partial pyrolysis of a mixture of  $(\text{H}_2\text{BNHCH}_3)_3$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  at  $110^\circ$  demonstrated that a compound having the properties expected for (A) is formed along with large amounts of



If the ionic species with 3 boron atoms is a precursor of the borazine ring, it would be the most reactive and present in very small quantities compared to the less

reactive species



Further evidence that the amine hydrochloride actually enters into the reaction is that the pyrolysis of a mixture of  $(\text{H}_2\text{BNHCH}_3)_3$  and  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$  at  $110^\circ$  gives a mixture of all the possible unsymmetrical borazines. The unsymmetrical borazines are not formed from the interaction of 1,3,5-trimethylborazine and  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$  at  $110^\circ$ . From the experimental evidence it appears that ring-closure via the borazine is more likely than by the polymerization of monomeric borazine.

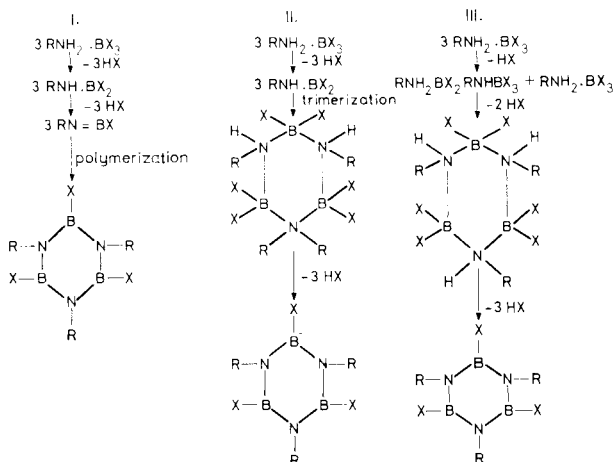
Let us now consider the various reaction paths leading to the formation of polyborazines by either dehydrogenation or dehydrohalogenation. It is clear from the foregoing discussion, that the 1 : 1 complex is a common intermediate in the polyborazine formation. In certain cases the adduct is not formed initially; from the work of Butcher and Gerrard [1] it may be postulated that, in the interaction of an alkylammonium chloride and boron trichloride, the 1 : 1 complex is formed by the decomposition of the initially formed alkylammonium tetrachloroborate:

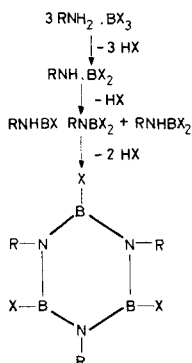


Similarly, Schaeffer *et al.* [4] showed that the 1 : 1 complex is formed from the interaction of lithium tetrahydroborate and trimethylammonium chloride in diethyl ether:

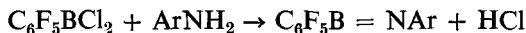


The possible reaction paths leading from the 1 : 1 complex stage to the polyborazine can be visualized as follows

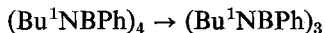




There is probably no single general reaction path for the polyborazines. Reaction path (i) involving formation of the borazine monomer ( $\text{RN} = \text{BX}$ ) was the first to be suggested. The formation of the monomeric borazine in the route to the borazine has received no experimental support. Only one borazine monomer has been reported by Pastzold and Simson [27]; an aromatic amine ( $\text{Ar} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{-}$ , mesityl) and dichloropentafluorophenyl borane were kept in boiling benzene for 2 days to yield the monomeric borazine:



but its conversion into borazine has not been reported. The reported (ii) conversion of tetramer quantitatively and irreversibly into trimer at  $250^\circ$  was demonstrated by differential thermal analysis (the monomeric borazine is a possible intermediate):



Lappet and Majumdar [8] postulated the formation of the borazine as an intermediate in the preparation of 1,3-di-*tert*-butyl-2,4-di-*tert*-butylamine-1,3-diaza-2,4-boretane. But it is indicated by the work of Beachley *et al.* [25, 26] and Currell *et al.* [24] that there is condensation leading to the formation of borazine.

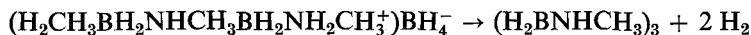
Beachley [25] heated methylamine borane at  $110^\circ$  and formed a complex:



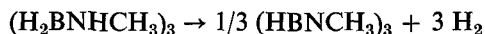
which on dehydrogenation yielded a condensation polymer:



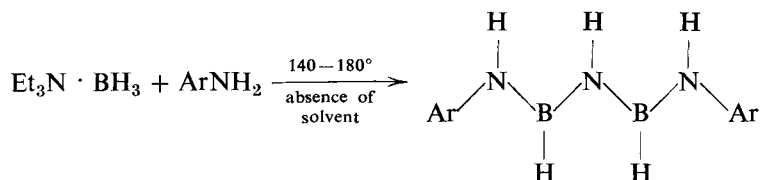
The latter compound cyclized to form N-methylamine borazane



Further heating resulted in loss of hydrogen with formation of borazine:



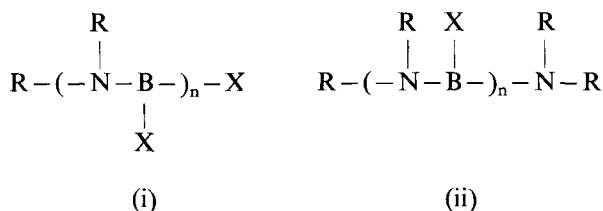
Currell *et al.* heated triethylamine borane and 2,6-dichloro-aniline and formed the boronamine:



When the boronamine was heated at 180–190° with triethylamine borane, condensation polymerization led to the formation of borazine:



Sheikh [28] heated the tetraalkylammonium haloborates and isolated the intermediate (i) in the formation of linear boron-nitrogen polymers having the structure (ii):



Polymers with these end-groups were not isolated in the ethyl system, but were obtained in the *n*-butyl system. It is possible that they were formed in the ethyl system but were not amenable to isolation.

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RÉSUMÉ — Cet article contient une revue des publications sur le mécanisme de formation des polymères de bore-azote.

ZUSAMMENFASSUNG — Dieser Artikel enthält eine Literaturübersicht über den Bildungsmechanismus anwendbarer Bor-Stickstoffpolymerer.

Резюме — Представлено литературное обозрение механизма реакций образования полимеров, содержащих связи бор — азот.