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Boron-Nitrogen Polymer Precursors

by

Y. S. Shaw, D.A. DuBois, R.H. Neilson*

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Fort Worth, Texas 76129

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Boron-Nitrogen Polymer Precursors

S. Yvette Shaw, Donn A. DuBois, and Robert H. Neilson*

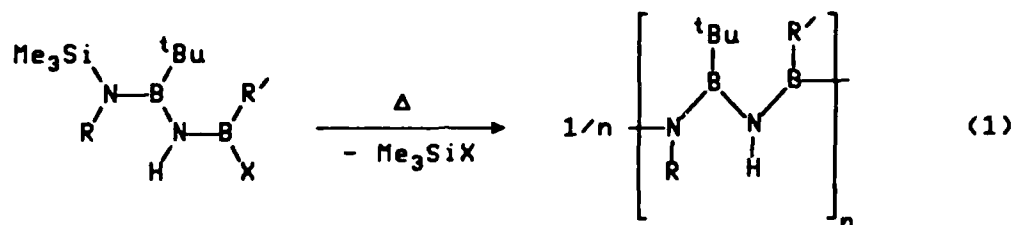
Department of Chemistry
Texas Christian University
Fort Worth, Texas 76129

The synthesis of tractable, linear B-N polymers $(\text{RBNR})_n$ is usually prevented by the ready formation of the extremely stable trimeric borazene ring system $(\text{RBNR})_3$. In an attempt to circumvent this problem, we have prepared a series

of new mono- and diborylamines, $\text{EN}(\text{CH}_2)_3\text{N}(\text{E}')\text{B}(\text{Ph})$ [$\text{E} = \text{H}$, $\text{E}' = \text{SiMe}_3$ (2), $\text{B}(\text{NMe}_2)_2$ (3), $\text{B}(\text{Ph})\text{NMe}_2$ (4); $\text{E} = \text{SiMe}_3$, $\text{E}' = \text{SiMe}_3$ (5), $\text{B}(\text{NMe}_2)_2$ (6), $\text{B}(\text{Ph})\text{NMe}_2$ (7); 8: $\text{E} = \text{E}' = \text{B}(\text{NMe}_2)_2$; 9: $\text{E} = \text{E}' = \text{SiMe}_2\text{H}$], by lithiation of the 1,3,2-diazaboracyclohexane ring system (1: $\text{E} = \text{E}' = \text{H}$) followed by quenching with electrophiles. The crystal and molecular structure of 8 has been determined by single crystal X-ray diffraction. Further chemistry of these compounds has been explored by reactions involving their pendent groups. For example, the bis(trimethylsilyl) compound 5 reacts with PhBCl_2 via Si-N bond cleavage to afford 11 [$\text{E} = \text{SiMe}_3$, $\text{E}' = \text{B}(\text{Ph})\text{Cl}$]. Also, the bis(dimethylamino)boryl derivative 8 undergoes transamination reactions with 1,3-diaminopropane to give compounds containing two (12) or three (13) BN_2C_3 rings linked together. Preliminary thermolysis studies show that some of the diborylamines (e.g., 3, 4, and 11) are potentially useful precursors to boron-nitrogen oligomers/polymers.

There has been considerable interest in recent years in the preparation of ceramic materials via pyrolysis chemistry of preceramic polymers. In particular, many important advances, most of which are described elsewhere in this Symposium volume, have been made in the synthesis of silicon carbide (SiC) and silicon nitride (Si_3N_4) from appropriate polymeric materials. As pointed out by Wynne and Rice [1], however, polymeric routes to boron nitride (BN), another important ceramic material, have been largely unexplored. This stems mainly from a lack of well characterized polymers containing boron and nitrogen. In the 1950s and 1960s, the syntheses of numerous amine- and aminoboranes were reported along with many unsuccessful attempts to polymerize such reagents. [2] The high thermal stability of the cyclic trimers [i.e., borazenes, $(\text{RBNR})_3$] is generally cited as the reason for the failure of the B-N "monomers" to polymerize. In fact, to our knowledge, all of the more recent attempts to prepare BN polymer precursors involve linking these borazene rings together to form cyclomatrix or at least cycloliner polymers. [3,4] Within this context, our main objective is to prepare and characterize tractable, high molecular weight, linear polymers containing the boron-nitrogen backbone. Aside from their potential as preceramic materials, the linear B-N polymers are expected to exhibit interesting and potentially useful properties themselves. For example, since they are the exact isoelectronic analogues of polyacetylene, these polymers should have similar electrical conductivity and possibly better physical/mechanical properties.

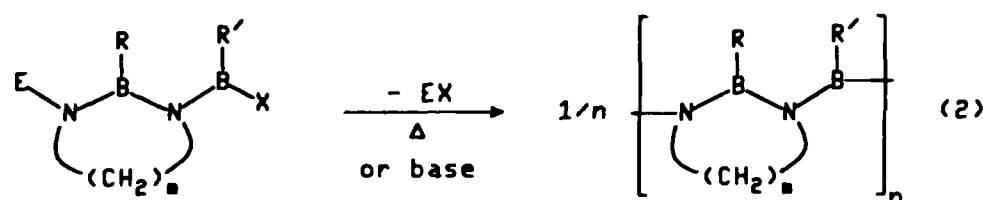
In order to overcome the problem of borazene ring formation, two different approaches, both involving diborylamines as condensation monomers, are being studied in our laboratory. The incorporation of a linear N-B-N-B unit along with other structural features should prevent these systems from condensing to the 6-membered borazene rings upon thermolysis. In the first method, acyclic diborylamines containing both the Si-N and the B-X groups (I) are the starting compounds. A few such species have recently been prepared and characterized. [5] In this case, the bulky t-Bu group on boron serves both to stabilize the primary aminoborane precursors to I and to help inhibit [6] formation of the borazene thermolysis products.



I: R, R', = Me, Et, t-Bu, Ph, etc.

X = Cl, NMe₂, OCH₂CF₃

The second approach involves linking the nitrogen atoms of the N-B-N-B backbone through bridging alkylene units by use of the 1,3,2-diazaboracycloalkane ring systems (II) (eq. 2). The bridges are intended to provide structural rigidity in order to prevent the boron-nitrogen backbone from condensing to the cyclic trimer. The alkylene moieties should also enhance the solubility of the polymeric products in organic solvents, thereby facilitating their characterization.



II: R, R', X = as in eq 1

E = H, SiMe₃

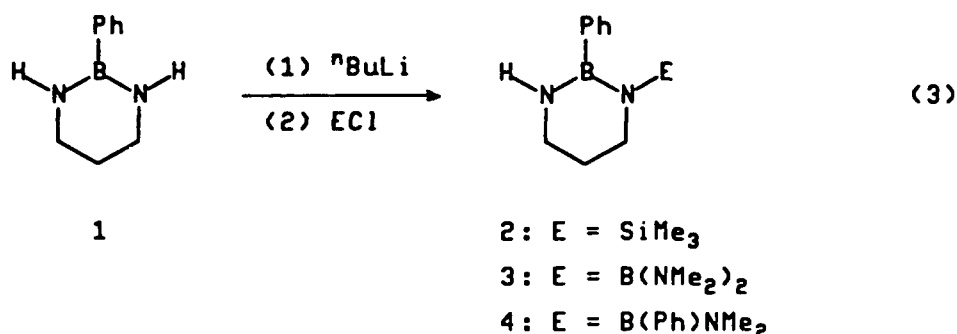
m = 2, 3, 4

We report here some of our recent results in the second of these areas. Specifically, the synthesis, structure, reactivity, and preliminary thermolysis studies of several new mono- and diborylamines based on the 2-phenyl-1,3,2-diazaboracyclohexane ring system (1) are described.

Results and Discussion

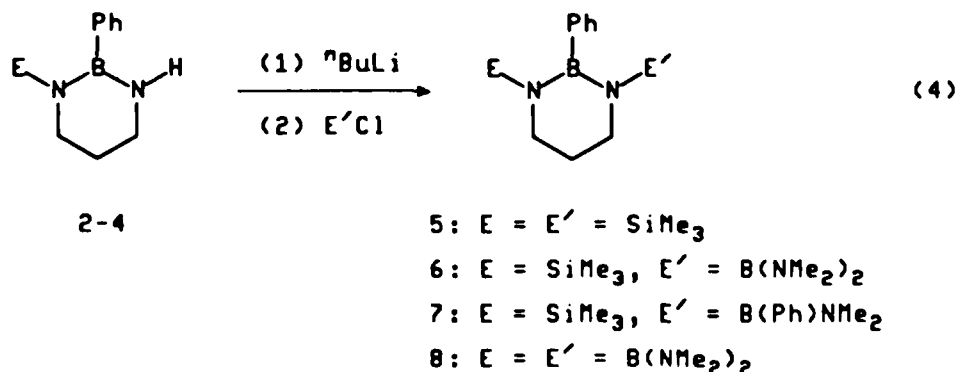
Synthesis. The 2-phenyl-1,3,2-diazaboracyclohexane ring system (1) was selected as the starting material in this study because: (1) it is prepared easily and in high yield by a three step synthesis from BCl_3 ; (2) the N-H bonds are potential sites for deprotonation and substitution reactions; and (3) the trimethylene bridge enhances the rigidity of the N-B-N backbone which should prevent cyclization upon thermolysis of an appropriate precursor.

The compounds described herein were prepared by three methods. The first route involves deprotonation/substitution at the N-H sites of 1, the second consists of a cleavage reaction of an Si-N derivative of 1 with PhBCl_2 , and the third route is a transamination reaction between a bis(dimethylamino)boryl derivative of 1 and an aliphatic diamine. In the first approach, compound 1 is deprotonated by treatment with one equivalent of $n\text{-BuLi}$. Quenching of the resulting anion with various electrophiles produces the monosubstituted products 2-4 (eq 3).



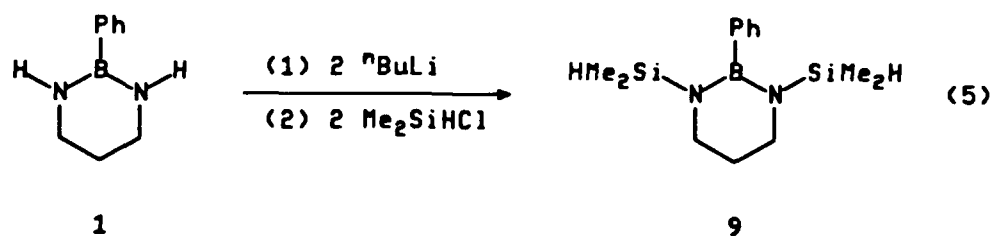
These new derivatives were isolated in good yields (60-94%) as high boiling liquids and were fully characterized by NMR spectroscopy (^1H , ^{13}C , and ^{11}B) and elemental analysis. The proton NMR of the starting material 1 shows a well-resolved multiplet and quintet for the trimethylene bridge. Upon monosubstitution, however, three complex multiplets are observed, indicative of the unsymmetrical structures of these derivatives. Also, the nonequivalence of the N-C carbon atoms is clearly apparent in the ^{13}C NMR spectra of 2-4.

Further substitution of the diazaboracyclohexane ring system may be accomplished by the same reaction sequence, starting with compounds 2-4, to afford the disubstituted products 5-8 (eq 4). The yields of these reactions ranged from 70 to 82%. The symmetrically

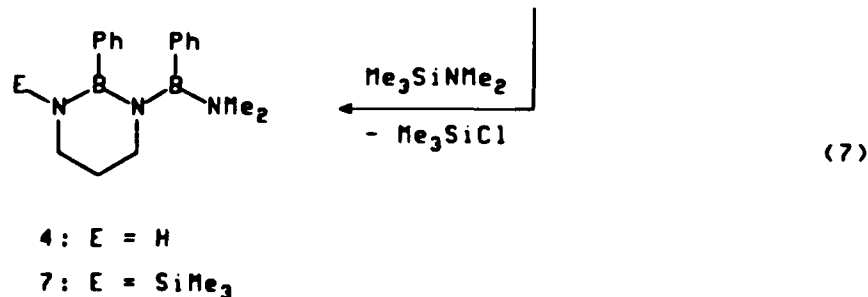
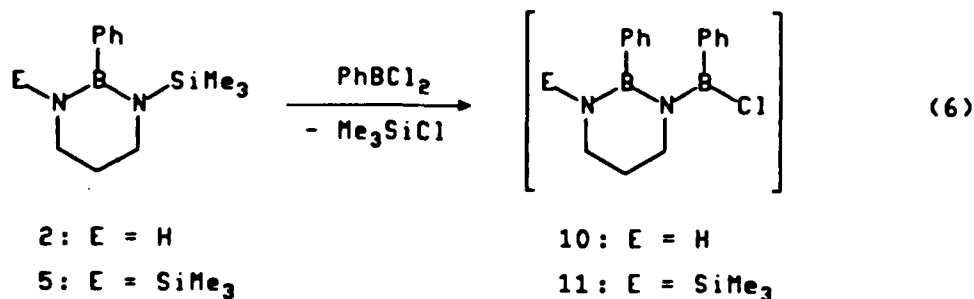


substituted compounds (5 and 8), like the starting material 1, exist as white crystalline solids while the mixed silyl/boryl derivatives 6 and 7 are clear liquids. Like their mono substituted analogues (2 and 3), the disilyl (5) and diboryl (8) derivatives are especially useful for further derivative chemistry. Furthermore, their ^1H NMR spectra are quite simple, consisting of a triplet/quintet pattern for the trimethylene bridge. Interestingly, both of the $-\text{B}(\text{Ph})\text{NMe}_2$ derivatives (4 and 7) exhibit nonequivalence of their N-methyl groups in the ^1H and ^{13}C NMR spectra, indicating that there are substantial barriers to rotation about the exocyclic B-N bonds in these systems. This observation is corroborated by the solid state structure of the crystalline compound 8 as described below.

As shown in equation 5, compound 1 may also be treated with two equivalents of $n\text{-BuLi}$ and disubstituted in one step by addition of HMe_2SiCl . Several attempts have been made to prepare the mono substituted (with the HMe_2Si group) product but mixtures of mono and disubstituted derivatives were obtained and could not be separated by fractional distillation.

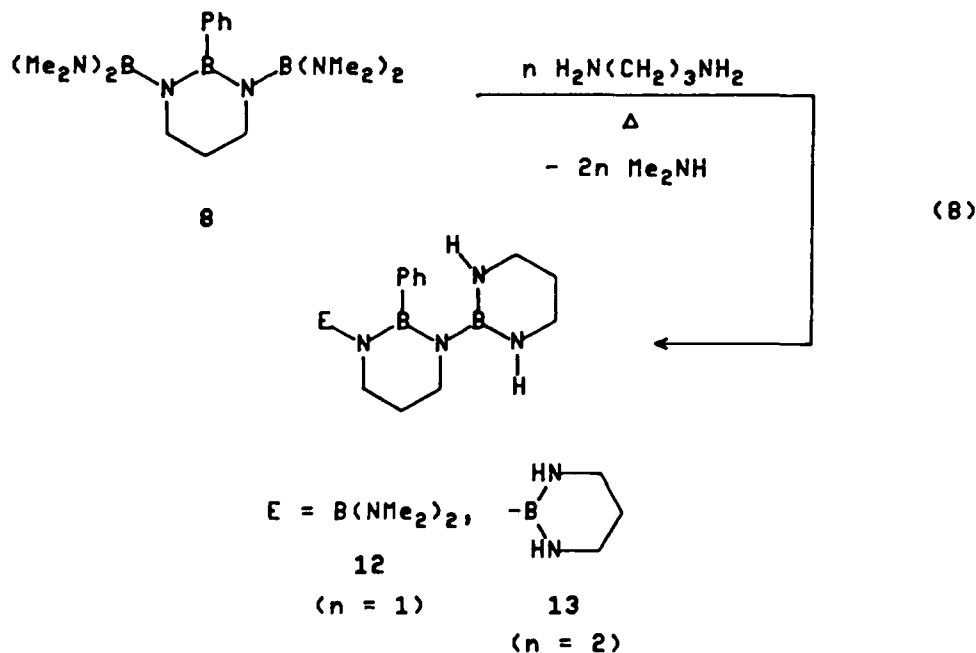


Other methods for derivatizing the diazaboracyclohexane ring system (1) are based on the reactivity of some of the pendent groups that have already been attached by the deprotonation/substitution method just described. For example, the mono and bis(trimethylsilyl) compounds, 2 and 5, undergo a facile silyl cleavage reaction with PhBCl_2 at 0°C in CH_2Cl_2 (eq 6) to form the reactive chloroborane derivatives 10 and 11. Unsuccessful attempts were made to isolate each of these intermediates. Upon solvent

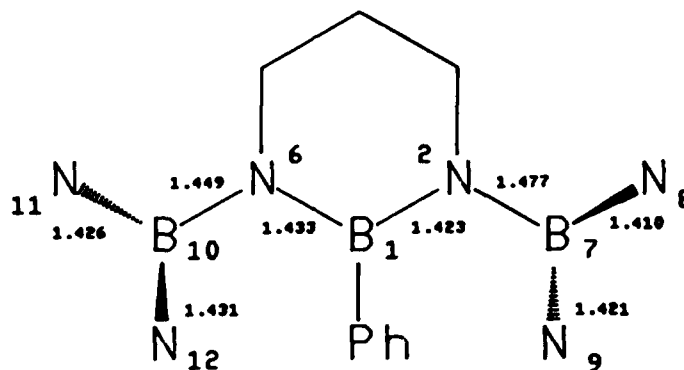


removal, 10 decomposed into an uncharacterizable solid residue, probably via HCl elimination since compounds containing both N-H and B-Cl bonds are inherently unstable. The N-silyl compound 11 was isolated in crude form as a yellow gum whose ^1H and ^{13}C NMR spectra are consistent with the proposed structure. The ^{11}B NMR spectrum, which is usually broad and featureless for compounds containing two or more boron atoms (e.g., 3, 4, 6, and 7), in this case consists of two distinct signals at 36.7 and 45.4 ppm. The nature of these intermediates was substantiated by another silyl cleavage reaction with $\text{Me}_3\text{SiNMe}_2$ to afford 4 and 7 (eq 7), which had been previously synthesized as shown above.

The third method that we have used to prepare these diazaboracyclohexane systems is the transamination reaction of 1,3-diaminopropane with the bis(dimethylamino)boryl compound 8 (eq 8). The solid products 12 and 13, which contain, respectively, two or three of the BN_2C_3 heterocycles linked by B-N bonds, could not be distilled (or crystallized), but they were thermally stable to at least 200°C . After minor impurities were removed from 12 by vacuum distillation and from 13 by washing with hexane, the structures were confirmed by ^1H , ^{13}C , and ^{11}B NMR spectroscopy.



Structure of Compound 8. Compound 8, the bis[is(dimethylamino)boryl] derivative of 1, was studied by single crystal X-ray diffraction and some of the general features of the molecular structure are reported here. This structure is significant since it contains a linear backbone of six B-N bonds and, as such, may serve as a close model for the structure of a linear high polymer. The diazaboracyclohexane ring is only slightly puckered with the phenyl group rotated out of the plane of the ring by 42.1° . A closer inspection of the BN skeleton (see figure below) shows that the backbone is essentially planar as expected. The atoms in the plane defined by B(10)-B(7) are coplanar with minor deviations at N(6) and B(10). The B-N bond lengths within this skeleton are characteristic of other aminoboranes and agree well with those of 1,8,10,9-triazaboradecalin. [8] However, the B-N bonds branching from the ring [i.e., N(6)-B(10) and N(2)-B(7)] are longer by 0.02-0.05 Å. Apparently, there is less dative π interaction within these bonds due to the rotation of the $\text{B}(\text{NMe}_2)_2$ moieties out of the plane of the



BN₂C₃ ring by approximately 57°. Furthermore, the bond length between N(2)-B(7) is 0.03 Å longer than that between N(6)-B(10) probably because of the twisted orientation of the phenyl substituent.

Preliminary Thermolysis Studies. A cursory survey of the thermal decomposition reactions of some of these potential B-N polymer precursors has been carried out. In several cases (e.g., the silylated diborylamines 6 and 7), the compounds were thermally stable for long periods at 200°C. Others, such as the N-H substituted diborylamines 3 and 4, show great promise as condensation monomers. When heated in sealed glass ampoules at 200°C for ca. one week, compounds 3 and 4 decomposed via elimination of Me₂NH (in the manner of eq 2) to yield thick oily residues. These materials were soluble in organic solvents including THF and, by size exclusion chromatography, were found to have molecular weights of ca. 5,500 - 6,000, which correspond to an average of about 25 repeat units (i.e., 50 B-N bonds) in the chain. In other experiments, the Si-N/B-Cl derivative 11 decomposed readily to give an orange solid residue (molecular weight ≈ 1,000) whose NMR spectra (¹H and ¹³C) are consistent with the type of condensation polymer shown in equation 2 (R = R' = Ph; m = 3). Thermal gravimetric analysis of this material showed an onset of decomposition at ca. 200°C, but, above 550°C, the residual weight was ca. 14% of the original value. This corresponds roughly to the amount of boron nitride that should be produced from this type of preceramic "polymer".

Conclusion

Thus far, this work has demonstrated three major polymer-related aspects of the chemistry of the 1,3,2-diazaboracyclohexane ring system. (1) A wide variety of mono- and disubstituted derivatives, including several novel diborylamines, can be easily prepared. (2) The structures of these small molecules, especially that of compound 8 with its rather long acyclic B-N skeleton, may be good models for the linear B-N polymers. (3) Based on some preliminary thermolysis studies, it appears that some of these derivatives will be useful as condensation monomers for the eventual synthesis of a high molecular weight B-N polymer. Our current efforts toward this objective include more detailed, systematic studies of variations in monomer structure, leaving groups, and thermolysis conditions.

Acknowledgments

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