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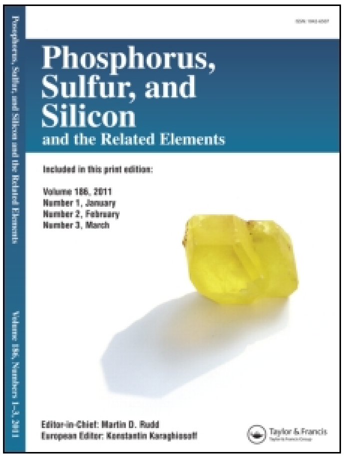

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Derivative Chemistry of the 1,3,2-Diazaboracyclohexane Ring System. Boron-Nitrogen Polymer Precursors

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DERIVATIVE CHEMISTRY OF THE 1,3,2-DIAZABORACYCLOHEXANE RING SYSTEM. BORON-NITROGEN POLYMER PRECURSORS

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Abstract. As part of a study of potential synthetic routes to tractable, linear B-N and/or B-N-P polymers, we have prepared a series of new N-silyl, N-boryl, and N-phosphoryl derivatives of the diazaboracyclohexane ring system. The synthesis, structure, dynamic stereochemistry, and some preliminary thermolysis studies of several of these compounds are reported.

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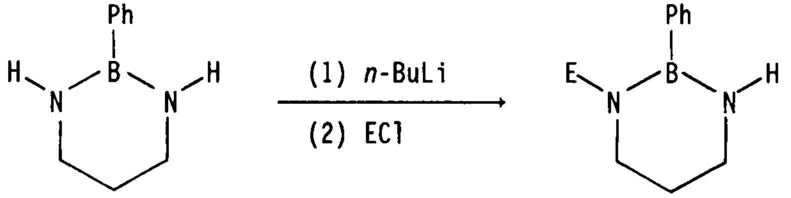
INTRODUCTION

In recent years, there has been an increasing level of interest in the use of small-molecule boron-nitrogen compounds as potential precursors to B-N polymers, BN-based ceramics, and other solid state materials.[1] The possibility of preparing *linear* B-N polymers [i.e., poly(iminoboranes),[2] $(RBNR)_n$] is especially intriguing since such materials are not only preceramic polymers[3] but are also the isoelectronic analogues of polyacetylene and related organic conductors. In the 1950's and 1960's, the syntheses of numerous amine- and aminoboranes were reported along with many unsuccessful attempts to polymerize such reagents.[4] The high thermal stability of the cyclic trimers [i.e., borazines, $(RBNR)_3$] is generally cited as the reason for the failure of the B-N "monomers" to polymerize. In order to overcome the problem of borazine ring formation, two different approaches, both of which involve the incorporation of a linear N-B-N-B unit and other structural features designed to prevent condensation to the six-membered borazine rings, are being studied in our laboratory. In the first method, acyclic diborylamines containing both Si-N and B-X groups are the starting compounds. A few such species, having the sterically protecting *t*-Bu group on boron, have already been reported.[5]

This paper is related to the second synthetic approach in which the nitrogen atoms of the N-B-N-B backbone are linked through bridging -$(CH_2)_n$- units by use of the 1,3,2-diazaboracycloalkane[6] ring systems. The bridges are intended to provide structural rigidity in order to prevent the boron-nitrogen backbone from condensing to the cyclic trimer. Specifically, we will summarize here some recent results on the preparative chemistry of N-Si, N-B, and N-P derivatives of the 1,3,2-diazaboracyclohexane ring systems.

RESULTS AND DISCUSSION

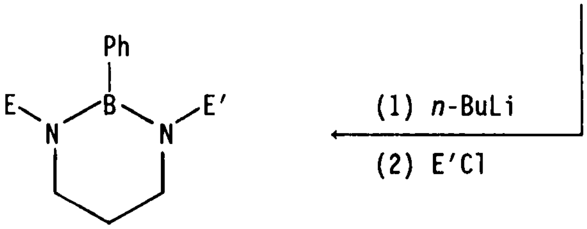
N-Silyl and N-Boryl Derivatives. The substitution of the N-H groups in the 1,3,2-diazabora-2-phenyl-cyclohexane ring system **1** is readily accomplished through deprotonation, by treatment with *n*-BuLi, followed by addition of an appropriate chlorosilane or chloroborane (eqs 1 and 2). In this manner, both mono- (**2**) and disubstituted (**3**) derivatives can be obtained as stable, distillable products with typical yields of 60 - 90%.



(1)

1

2: E = $SiMe_3$, $B(NMe_2)_2$, $B(Ph)NMe_2$



(2)

3: E = $SiMe_3$; E' = $SiMe_3$, $B(NMe_2)_2$, $B(Ph)NMe_2$
E = E' = $B(NMe_2)_2$

The structure and dynamic stereochemistry of some of these compounds have been studied and reported in preliminary form.[7,8] The bis[bis(dimethylamino)boryl] deriva-

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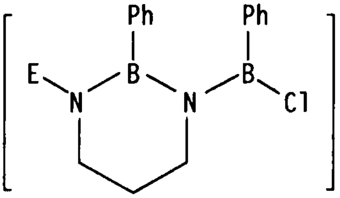
tive [**3**: E = E′ = B$(NMe_2)_2$], which has been studied by X-ray crystallography,[8] is of interest as a structural model for a linear B-N polymer since its backbone consists of a linear array of six B-N bonds. The planar BN framework is consistent with sp^2 hybridization at both boron and nitrogen. Although all of the B-N bond lengths within this skeleton are similar to those of other aminoboranes, the bonds branching from the ring are longer than those within the ring by 0.02-0.05 Å. Apparently, there is less dative π interaction within these bonds due to the rotation of the $B(NMe_2)_2$ moieties out of the plane of the BN_2C_3 ring by approximately 57°.

The ground state structures of some of the N-boryl derivatives **2** and **3** were determined by variable temperature ^1H NMR measurements and found to be completely consistent with the solid state structure. The ^1H NMR spectra of **2** and **3** revealed a temperature dependence similar to that observed previously for the related compounds, $(Me_3Si)_2NB(X)NMe_2$ (X = Cl, Ph, NH_2, alkyl).[9] For example, at room temperature, the NMe_2 protons of the -B(Ph)NMe_2 derivative **2** are nonequivalent as a result of restricted rotation about the B-NMe_2 bond. Compound **3** [E = E′ = $B(NMe_2)_2$] exhibits a similar splitting of the NMe_2 signal at lower temperatures. The free energies of activation ($\Delta G^{\ddagger}$), determined by measurement of the coalescence temperatures, were found to be 17.3 and 12.9 kcal/mol, respectively. The value observed for **2** is, in fact, typical of aminoboranes in which only one nitrogen is oriented properly for π-bonding to boron,[9] indicative of a lowering of the B-N π bond order due to competition of two nitrogen electron pairs for the empty *p* orbital of boron.[9]

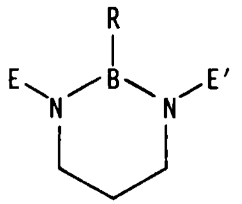
The substituted diazaboracyclohexane ring system **2** and **3** may be further derivatized by reactions of some of the pendant functional groups. For example, the mono- and bis(trimethylsilyl) compounds undergo smooth silyl cleavage reactions with $PhBCl_2$ to afford the thermally unstable chloroboranes **4**. Treatment of these B-Cl compounds with Me_3SiNMe_2 yields the B-NMe_2 derivatives (see **2** and **3** above). The N-$SiMe_3$ compound **4**



4: E = H, $SiMe_3$

is isolated in crude form as a cloudy yellow gum. The ^{11}B NMR spectrum, which is usually a broad and featureless signal for similar compounds containing two or more boron atoms, consists of two distinct signals at 36.7 and 45.4 ppm. On heating, this compound readily eliminates Me_3SiCl to give an orange solid residue that, by gel permeation chromatography has a molecular weight of ca. 6,000. This corresponds to an average chain length of about 25 - 30 repeat units in an oligomeric structure, $[\text{-}\overline{\text{N-B(Ph)-N}}\text{-B(Ph)-}]_n$. A few of the other precursors [e.g., **2**: E = $B(NMe_2)_2$, $B(Ph)NMe_2$] give similar oligomeric/polymeric products upon thermolysis. These condensation processes are currently being studied in more detail and the results will be reported in due course.

In other recent work, we are attempting to stabilize some of these potential polymer precursors by incorporating more sterically hindering groups at boron and/or nitrogen. Using synthetic methodology similar to that described above, a variety of B-*i*-propyl analogues **5** and N-$SiMe_2$(*t*-Bu) derivatives **6** are accessible. These more hindered systems [e.g., **5**: E′ = $B(Ph)OCH_2CF_3$ and **6**: E′ = B(Ph)Cl] are usually distillable liquids and, thus, are more thermally stable than their simple B-phenyl analogues.



5: R = *i*-Pr; E = H, $SiMe_3$;
E′ = $SiMe_3$, $SiMe_2H$, $B(NMe_2)_2$, $B(Ph)NMe_2$, $B(Ph)OCH_2CF_3$

6: E = $SiMe_2$(*t*-Bu); R = Ph; E′ = H, $B(Ph)OCH_2CF_3$, B(Ph)Cl

Phosphorus Derivatives. The condensation polymerization of appropriate N-silylphosphoranimines, $Me_3SiN{=}P(X)RR'$, is an efficient method of preparing a class of phosphazenes, the poly(alkyl/arylphosphazenes), $[R_2PN]_n$, that are not accessible by other synthetic approaches.[10] The overall scope of this process, the preparative chemistry of the Si-N-P precursors, and the nature of the phosphazene products (e.g., polymeric and/or cyclic) that it affords are all under active investigation. The success of this type of condensation polymerization in the phosphazene area has led us to investigate the possibility of applying it to the synthesis of other inorganic polymer systems. These include the poly(imino-

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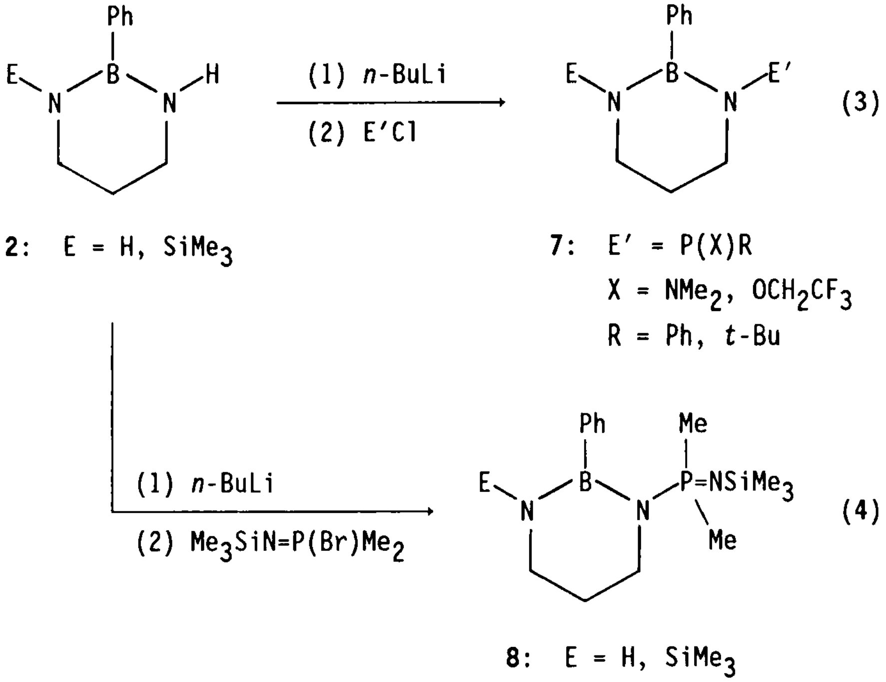
boranes) discussed above and, more recently, some B-N-P compounds which are briefly noted here.

The N-lithio derivatives of the 1,3,2-diazabora-2-phenyl-cyclohexane ring systems can also be treated with various P^{III} (eq 3) and P^{V} (eq 4) electrophiles to afford the novel P-N derivatives **7** and **8**, respectively. These products are generally obtained as distillable liquids in moderate to good yields (50 - 85%) and are readily characterized by multinuclear NMR spectroscopy and elemental analysis. Full details of the synthesis, characterization, and reactivity of these and related compounds will be published in forthcoming papers.



2: E = H, $SiMe_3$

7: E′ = P(X)R
X = NMe_2, OCH_2CF_3
R = Ph, *t*-Bu

8: E = H, $SiMe_3$

Most of this work, especially that on the B-N-P systems, is in its preliminary stages involving the synthesis of many types of new compounds and the development of new synthetic methods. Future efforts will then be more directly focused on specific types of B-N and/or B-N-P polymers, cyclic analogues, and their appropriate precursors.

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