Bull. Chem. Soc. Ethiop. **1999**, 13(2), 121-125.
Printed in Ethiopia

ISSN 1011-3294
© 1999 Chemical Society of Ethiopia

SYNTHESIS AND CHARACTERIZATION OF SOME DERIVATIVES OF 2-t-BUTYL-1,3,2-DIAZABORACYCLOPENTANE RING SYSTEM

Negussie Retta[1*] and Robert H. Neilson[2]

[1]Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia
[2]Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

(Received September 2,1999; revised October 19, 1999)

ABSTRACT. Eight new mono- and disubstituted 2-t-butyl-1,3,2-diazaboracyclopentane, $EN(CH_2)_2E'NB^tBu$ derivatives, (E = H, E' = H (**I**); E = $SiMe_2H$ (**II**); $SiMe_2Cl$ (**III**); $SiMe_2NH_2$ (**IV**); E = $SiMe_3$ (**V**); E = E' = $SiMe_2H$ (**VI**); E' = $SiMe_2Cl$ (**VII**); and E' = $SiMe_2NH_2$ (**VIII**); have been synthesized in good yield and characterized by spectroscopic and elemental analysis. ^{13}C and ^1H NMR spectral data are analyzed and discussed.

INTRODUCTION

In recent years, there has been increasing interest in small molecule boron-nitrogen compounds as potential precursors to B-N polymers [1], B-N based ceramics and other solid state materials [2].

Ceramics such as borides in one or more crystalline modifications are known for their high mechanical strength, hardness, corrosion resistance, oxidation resistance, thermal shock stability and wide variation in electrical properties [3]. However, the difficulties encountered in the preparation of linear B-N polymers [i.e., poly(iminoboranes), $(RBNR)_n$] with well-defined bulk properties, grain characteristics and microstructures have hampered the advance in the field [2].

In the 1950s and 1960s, 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 circumvent the borazine ring formation, the nitrogen atoms of the -N-B-N- backbone have been linked by $-(CH_2)_3-$ units [1,5]. The bridge is intended to provide structural rigidity in order to prevent the boron-nitrogen backbone from condensing to the cyclic trimers. We have now extended this work by using $-(CH_2)_2-$ as the bridging unit and report new mono- and di-substituted 1,3,2-diazaboracyclopentane prepolymer compounds.

EXPERIMENTAL

General. The following reagents were obtained from commercial sources and used without purification: nBuLi (Aldrich), BCl_3 (Petrarch System Inc) Me_2NH (Matheson), ^tBuLi (Aldrich), ethylenediamine (Mallinckrodt), Me_3SiCl (Petrarch System Inc), Me_2SiHCl (Petrarch System Inc), Me_2SiCl_2 (Petrarch System Inc), NH_3 (Big Three Ind. Inc). Solvents such as Et_2O, hexane and pentane were distilled from CaH_2 prior to use and all manipulations during synthesis have been by Schlenk tube techniques.

Proton and $^{13}C\{H\}$ spectra were recorded on a Varian XL 300 Spectrometer with $SiMe_4$ and $CDCl_3$, respectively, as references. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

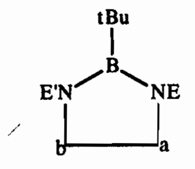
Procedure

1,3,2-diazabora-2-t-butylcyclopentane, $HN(CH_2)_2HNB^tBu$ (**I**). The compound was made by refluxing $^tBuB(NMe_2)_2$ (2.5 g, 160 mmol) in hexane (100 mL) and ethylenediamine (1.1 g, 18 mmol) for 5 h and stirring the mixture overnight. The residue, after stripping off the solvent, was distilled to give the desired product as a colorless liquid. B.P.: 48-49 °C/13 mm Hg; yield: 87%. δ ^1H: 0.72 (9H, ^tBu, s), 3.14 (4H, CH_2, s), 2.4 (2H, NH, b); δ $^{13}C\{H\}$: 28.57 (^tBu, s), 44.46 (CH_2, s).

1,3,2-diazabora-2-t-butyl-3-(dimethylsilyl)cyclopentane, $HN(CH_2)_2SiMe_2HNB^tBu$ (**II**). The target compound was made from the lithiated compound **I** (2.5 g, 19.84 mmol) and Me_2SiCl (1.1 g, 19.84 mmol) in Et_2O (*10 mL*) as a colorless liquid. B.P.: 68-73 °C/10 mm Hg; yield: 2.8 g, 78%. δ ^1H: 0.08 (6H, SiMe, d, J = 2.4 Hz), 0.87 (9H, ^tBu, s), 4.65 (1H, SiH, sp, J = 3.4 Hz), 4.70 ($2H^a$, (see footnote), dt, ^1J = 3.3, ^2J = 0.91 Hz), 3.18 ($2H^b$, m), 3.14-3.0 (NH, b); δ $^{13}C\{H\}$: -1.59 (SiMe, s), 29.04 (^tBu, s), 47.58 (C^a, s), 44.05 (C^b, s).

1,3,2-diazabora-2-t-butyl-3-(chlorodimethylsilyl)cyclopentane, $HN(CH_2)_2SiMe_2ClNB^tBu$ (**III**). To a solution of the lithium derivative of compound **I** (made from 2.5 g, 19.05 mmol of **I** and 7.6 mL of 2.5 M BuLi, 19.05 mmol) in Et_2O (100 mL) Me_2SiCl_2 (2.5 g, 19.05 mmol) in Et_2O (20 mL) was added dropwise maintaining the temperature at 0 °C. The mixture was stirred overnight at room temperature. The usual work-up gave the desired product. B.P.: 53-54 °C/0.3 mm Hg; yield: 2.8 g, 67%. Anal., calcd. (found) *for* $C_8H_{24}BN_2SiCl$: C, 43.95 (44.18); H, 9.22 (9.27). δ ^1H: 051 (6H, SiMe, s), 0.88 (9H, ^tBu, s), 3.39 ($2H^a$, t, J = 7.7 Hz), 3.13 ($2H^b$, dt, J_1 = 8.9; J_2 = 1.2 Hz), 3.18-3.05 (1H, NH, b); δ $^{13}C\{H\}$: 5.49 (SiMe, s), 29.36 (^tBu , s), 49.84 (C^a, s), 43.40.96 (C^b, s).

1,3,2-diazabora-2-t-butyl-3-(aminodimethylsilyl)cyclopentane, $HN(CH_2)_2SiMe_2NH_2NB^tBu$ (**IV**). A 250 mL 3-necked flask equipped with a dropping funnel, stirrer and septum was charged with hexane (100 mL) cooled to -78 °C. Liquid NH_3 (*ca* 1.0 mL, 16.5 mmol) was added to the cooled flask via a funnel. The chlorosilyl derivative (**III**) (1.2 g, 5.5 mmol) in hexane (10 mL) was added dropwise and the mixture was allowed to warm to room temperature then stirred overnight. The usual work-up gave a colorless product. B.P.: 50-54 °C/6 mm Hg; yield: 0.7 g, 79%. Anal,, calcd.(found) for $C_8H_{22}BN_3Si$: C, 48.24 (48.01); H, 11.13 (11.00). δ ^1H: 0.78 (6H, SiMe, s), -0.03 (9H, ^tBu, s), 3.19 (4H, CH_2, s), 2.35-2.58 (1H, NH, b), 0.69 (2H, NH_2, b); δ $^{13}C\{H\}$: 4.21 (SiMe, s), 28.70 (^tBu, s), 44.59 (CH_2, s).



E and E' are electrophiles

1,3,2-diazabora-2-t-butyl-3-(trimethylsilyl)cyclopentane, $Me_3SiN(CH_2)_2NHB^tBu$ (**V**). The compound was made from **I** (2.5 g, 19.84 mmol) in Et_2O (100 mL), TMEDA (3.0 mL, 20 mmol), BuLi (9 mL of 2.5 M, 19.84 mmol) and Me_3SiCl (2.1 g 19.84 mmol) in Et_2O (10 mL) after the usual work-up. B.P: 68-70 °C/5 mm Hg; yield: 2.4 g, 62%. Anal., calcd.(found) for $C_9H_{22}BN_2Si$: C, 54.54 (54.18); H, 11.70 (12.06); δ ^{1}H: 0.10 (9H, $SiMe_3$, s), 0.85 (9H, ^{t}Bu, s), 3.27 (2H^a, dt, J_1 = 8.0, J_2 = 1.2 Hz), 3.09 (2H^b, t, J = 7.4 Hz) 2.9 (1H, NH, b); δ ^{13}C{H}: 2.47 (Me_3Si, s), 29.75 (^{t}Bu, s), 50.17 (C^a, s), 43.79 (C^b, s).

1,3,2-diazabora-2-t-butyl-1,3-bis(dimethylsilyl)cyclopentane, $Me_2SiHN(CH_2)_2SiMe_2HNB^tBu$ (**VI**). A solution of Me_2SiClH (3.02 g, 31.74 mmol) in Et_2O (20 mL) was slowly added to the dilithium derivative of **I** made from (2.0 g, 15.87 mmol of **I** and BuLi,12.7 mL of 2.5 M solution, 31.74 mmol) and the mixture left stirring overnight. The usual work-up and distillation gave the analytically pure compound as a colorless liquid. B.P.: 53-54 °C/0.3 mm Hg; yield: 3.0 g, 78%. Anal., calcd.(found) for $C_{10}H_{27}BN_2Si_2$: C, 49.57 (49.47); H, 11.13 (11.10). δ ^{1}H: 0.12 (12H, SiMe, d, J = 3.3 Hz), 1.01 (9H, ^{t}Bu, s), 3.09 (4H, CH_2, s), 4.81 (2H, SiH, sp, J = 3.3 Hz); δ ^{13}C{H}: 0.68 (SiMe, s), 30.77 (^{t}Bu, s), 48.29 (CH_2, s).

1,3,2-diazabora-2-t-butyl-1-dimethyl-3-(chlorodimethylsilyl)cyclopemtane,

$Me_2HSiN(CH_2)_2SiMe_2ClNB^tBu$ (**VII**). Compound **II** (1.2 g, 6.5 mmol) in Et_2O (100 mL) was treated with BuLi (2.6 mL of 2.5 M, 6.5 mmol) at 0 °C followed by Me_2SiCl_2 (0.84 g, 6.5 mmol) in Et_2O (10 mL) to give the desired product as a colorless liquid. B.P.: 59-60 °C/0.1 mm Hg; yield: 88%, Anal., calcd.(found) for $C_{10}H_{26}BN_2Si_2Cl$: C, 43.40 (43.43); H, 9.47 (9.23). δ ^{1}H: 0.53 (6H, SiMeCl, s) 0.12 (6H, SiMeH, d, J = 3.25 Hz), 1.00 (9H, ^{t}Bu, s), 3.02 (2H^a, t, J = 7.0 Hz), 3.27 (2H^b, t, J = 3.2 Hz), 4.82 (1H, SiH, sp, J = 3.2 Hz); δ ^{13}C{H}: -1.09 ($SiMe_2H$, s), 6.62 (SiMeCl, s), 30.74 (^{t}Bu, s), 47.57 (C^a, s), 50.13 (C^b, s).

1,3,2-diazabora-2-t-butyl-1-dimethylsilyl-3-(aminodimethylsilyl)cyclohexane,

$Me_2HSiN(CH_2)_2SiMe_2NH_2NB^tBu$ (**VIII**). The compound was made from compound **VII**

$Me_2Si(H)N(CH_2)_2SiMe_2ClNB^tBu$ (2.9 g, 13.36 mmol) in hexane (15 mL) and NH_3 (1.14g, 66.8 mmol) following the procedure given for the synthesis of **IV**. Further work-up gave a colorless product in 90% purity shown by ^{1}H NMR. B.P.: 79-81 °C/0.8 mm Hg; yield: 1.5 g, 44%. δ ^{1}H: 0.085 (6H, SiMeH, d, J = 3.3 Hz), 0.98 (9H, ^{t}Bu, s), 0.13 (6H, $SiMeNH_2$, s), 3.0 (2H^a, t, J = 7.6 Hz), 3.17 (2H^b, t, J = 8.35 Hz), 0.75 (2H, NH, b), 4.79 (1H, SiH, sp, J = 3.2 Hz); δ ^{13}C{H}: 3.26 ($SiMeNH_2$, s), -0.98 (SiMeH, s), 30.86 (^{t}Bu, s), 47.60 (C^a, s), 50.10 (C^b, s).

RESULTS AND DISCUSSION

The synthesis of the 2-t-butyl-1,3,2-diazaboralidene, $HN(CH_2)_2NHB^tBu$ (**I**), by the transamination of bis(dimethylamino)-t-butylborane and ethylenediamine (see reaction given below) is easy and gives a good yield (*ca* 87%).

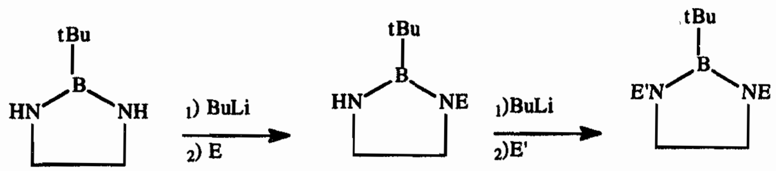
$$BCl_3 + 6Me_2NH \xrightarrow[\text{hexane}]{-78^{o}} B(NMe)_3 + Me_2NHCl$$

$$B(NMe_2)_3 + 1/2\,BCl_3 \xrightarrow[\text{pentane}]{-78^{o}} 3/2\,ClB(NMe_2)_2$$

$$ClB(NMe_2)_2 + {}^{t}BuLi/Et_2O \xrightarrow[\text{hexane}]{-78^{o}} {}^{t}BuB(NMe_2)_2$$

$${}^{t}BuB(NMe_2)_2 + H_2N(CH_2)_2NH_2 \rightarrow I$$

The NH bonds of the diazaboracyclopentane are potential sites for deprotanation by treatment with an equimolar amount of BuLi and subsequent addition of the appropriate electrophiles (E and/or E') gave the desired derivatives.



E and E' are electrophiles

These new derivatives were isolated in good yield (62 - 88%) as high boiling liquids and were fully characterized by NMR spectroscopy (^{1}H and ^{13}C) and elemental analyses. The elemental analyses and spectral data cited in the experimental section for each derivative seem to indicate consistency with the proposed structure.

The ^{1}H NMR spectra of the starting compound (**I**) shows protons, a singlet at δ 3.14 for the methylene protons, a singlet at δ 2.40 for the protons on the nitrogen and a singlet at δ 0.72 for the ^{t}Bu protons. Upon monosubstitution, however, a triplet and doublet of triplets were observed, indicating the non-equivalence of the two methylene protons. Also the non-equivalence of the N-C carbon atoms are clearly apparent in the ^{13}C NMR. This was not observed in compound **IV** where the methylene protons appear as a singlet at δ 3.19. In the 1,3,2-diazabora-2-^{t}butyl-3-dimethylsilylaminecyclohexane (where the bridging group is -$(CH_2)_3$-, the methylene protons are non-equivalent and the protons and the carbons of the silyl group are at much lower field (δ = 0.06 and 2.22, respectively) indicating more shielding [5]. The symmetrical compound like **VI** show a singlet for the two methylene protons in the ^{1}H NMR and the same is observed in the ^{13}C NMR.

Mono substitution has invariably caused a low field shift of the methylene proton adjacent to the substitution site due to the deshielding effect of the substitutent, the most pronounced of these being in **II** followed by **III**. The effect on the ^{t}Bu is not remarkable except in the di-substituted derivatives where deshielding is also noticed.

The synthesis of compound **II** from compound **I** and Me_2SiClH gave mixtures containing about 6% of the di-substituted derivative **VI** and 94% of the mono-derivative **II** that could not be separated by fractional distillation. When these mixtures were treated with one equivalent of nBuLi followed by the addition of Me_2SiHCl, the usual work-up gave compound **VII** in analytically pure form.

Compound **VI** was made by treatment of **I** with two equivalents of n-BuLi followed by the addition of $SiMe_2HCl$ and obtained analytically pure product. Similarly, the preparation of compound **VIII** from compound **VII** and liquid NH_3 at -78 °C gave the target compound **VIII** together with compounds **IV** and **I** with the overall yield of 10%.

ACKNOWLEDGMENT

RHN thanks the U.S. Office of Naval Research, the Robert A. Welch Foundation and the TCU Research Fund for financial support.

REFERENCES

1. Shaw, S.Y.; Dubios, D.A.; Watson, W.H; Neilson, R.H. *Inorg. Chem.* **1988** , 27, 974.
2. Paine, R.T., Narula, C.K., *Chem. Rev.* **1990**, 90,73 (and references therein).
3. Kingery, W.D., Bowen, H.K., Ullman, D.R., *Introduction to Ceramic*, 2nd ed., Wiley: New York; 1976.
4. Atkinsen, I.R., Currell, B.R., *Inorg. Macromol. Rev.* **1971**, 1, 203.
5. Retta, N.; Neilson, R.H. *Bull. Chem. Soc. Ethiop.* **1999**, 13, 51.