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

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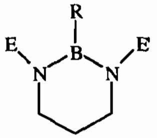
ABSTRACT. New mono and disubstituted 2-t-butyl-1,3,2-diazaboracyclohexane, $E\overline{N(CH_2)_3E'N}B^tBu$ derivatives, E = H, E' = H (I), $SiMe_2H$ (II), $SiMe_2Cl$ (III), $SiMe_2NH_2$ (IV); E = $SiMe_3$, E' = $SiMe_2Cl$ (V), E = $SiMe_2H$, E' = $SiMe_2H$ (VI), $SiMe_2NH_2$ (VII), and $SiMe_2Cl$ (VIII), 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

There has been considerable interest in recent years in the preparation and characterization of tractable, high molecular weight linear polymers containing the B-N backbone. Aside from their potential as preceramic materials, the linear B-N polymers are expected to exhibit useful properties in material science.

However, significant advances in the area have been hampered from a lack of suitable polymeric routes. The high thermal stability of the cyclic trimers, i.e. borazenes, $(RBNR)_3$ is generally cited as the reason for the failure of the B-N monomers to polymerize [1]. In order to overcome the problem of borazine ring formation upon thermolysis of the B-N monomers, the E-N-B-N-E' systems of the monomerses have been linked through bridging alkylene units to give 1,3,2-diazaboracycloalkane ring system [2].



R = Ph or iPr
E and E are electrophiles

The bridge is intended to provide structural rigidity in order to prevent the boron-nitrogen back-bone from condensing to the cyclic trimer. In recent years some potentially reactive monomers where R= Ph or ^{i}Pr have been synthesized and characterized [1,3]. Here we report the synthesis and characterization of additional new derivatives with R = ^{t}Bu.

EXPERIMENTAL

General. The following reagents were obtained from commercial sources and used without purification: nBuLi (Aldrich), Me_3SiNMe_2 (Aldrich), ^{t}BuLi (Aldrich), 1,3- propylenediamine (Aldrich), Me_3SiCl (Petrarch System Inc), Me_2SiHCl (Petrarch System Inc), Me_2SiCl_2

(Petrarch System Inc), NH_3 (Big Three Ind. Inc), BCl_3 (Petrarch System Inc), and Me_2NH (Matheson). 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.

$HN(CH_2)_3NHB^tBu$ (I) was prepared according to the known procedure [4]. 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 Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Procedure

1,3,2-diazabora-2-t-butyl-3-(dimethylsilyl)cyclohexane, $HN(CH_2)_3SiMe_2HNB^tBu$ (**II**). A 250 mL 3-necked flask equipped with a dropping funnel, stirrer, and septum was charged with the compound (**I**) (3.0 g, 21.4 mmol) in Et_2O (100 mL). nBuLi (21.4 mmol, 8.6 mL of 2.5 M solution in hexane) was added dropwise maintaining the temperature at 0 °C and the mixture was stirred for 2 h at 0 °C and for a further of 2 h at room temperature.

Me_2SiClH (2.2 g, 21.4 mmol, 2.6 mL) in Et_2O (10 mL) was slowly added to the cooled solution (at 0 °C). The mixture was then left stirring overnight at room temperature, Et_2O removed, the residue extracted with hexane, the extract filtered, hexane stripped from the filtrate and the residue distilled at 55 - 60 °C/4 mm Hg to give the analytically pure colorless liquid. Yield: 2.8 g, 67%. Anal., calcd (found) for $C_9H_{23}BN_2Si$: C, 54.54 (54.33); H, 11.70 (12.02). δ ^1H: 0.06 (6H, SiMe, d, J = 3.3 Hz), 0.86 (9H, ^tBu, s), 4.87 (1H, SiH, sp, J = 3.20 Hz), 2.84 ($2H^a$, (see footnote) t, J = 5.1 Hz), 1.59 ($2H^b$, m, J = 6.5 Hz), 2.92 ($2H^c$, m, J = 6.0, 2.6 Hz), 3.14-3.0 (NH, b); δ $^{13}C\{H\}$: -1.87 (SiMe, s), 29.46 (^tBu, s), 40.25 (C^a, s), 28.01 (C^b, s), 41.98 (C^c, s).

1,3,2-diazabora-2-t-butyl-3-(chlorodimethylsilyl)cyclohexane, $HN(CH_2)_3SiMe_2ClNB^tBu$ (**III**). To a solution of the lithium derivative of compound (**I**) (made from 2.5 g, 17.9 mmol of compound **I** and 7.2 mL of 2.5 M BuLi) in Et_2O (100 mL). Me_2SiCl_2 (2.3 g 17.9 mmol) in Et_2O (20 mL) was added dropwise maintaining the temperature at 0 °C. The mixture was then left stirring overnight at room temperature. The usual workup gave the desired product. B.P.: 49-50 °C/0.01 4 mm Hg; yield: 2.0 g, 48%. Anal., calcd. (found) for $C_9H_{27}BN_2SiCl$: C, 46.47 (46.53); H, 9.53 (9.50). δ ^1H: 052 (6H, SiMe, s), 0.85 (9H, ^tBu, s), 1.65 ($2H^a$, m), 2.93 ($2H^b$, m), 3.03 ($2H^c$, m), 3.32-3.38 (1H, NH, b); δ $^{13}C\{H\}$: 6.58 (SiMe, s), 29.95 (^tBu, s), 40.02 (C^a, s), 27.96 (C^b, s), 43.67 (C^c, s).

1,3,2-diazabora-2-t-butyl-3-(aminodimethylsilyl)cyclohexane, $HN(CH_2)_3SiMe_2NH_2NB^tBu$ (**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 from a cylinder (1.8 g, 2.5 mL, 53.75 mmol) was added to the cooled flask via a funnel. The chlorosilyl derivative (**III**) (2.5 g, 10.75 mmol) in hexane (20 mL) was added dropwise and the mixture was allowed to

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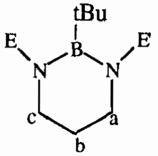


warm to room temperature then stirred overnight. The usual workup gave a colorless product. B.P.: 53.54 °C/0.2 mm Hg; yield: 1.6 g, 72%. Anal., calcd.(found) for $C_9H_{27}BN_3Si$: C, 50.70 (50.94); H, 11.35 (11.42). δ ^{1}H: 0.06 (6H, SiMe, s), 0.83 (9H, ^{t}Bu, s), 1.65 (2H^a, m), 3.05-3.15 (1H, NH, b); 2.91-2.83 (4H^b and H^c, m), 1.54 (2H^a, m), 0.76-0.67 (2H, NH_2, b). δ ^{13}C{H}: 2.22 (SiMe, s), 30.11 (^{t}Bu, s), 40.28 (C^a, s), 28.42 (C^b, s), 43.28 (C^c, s).

1,3,2-diazabora-2-t-butyl-1-trimethylsilyl-3-(chlorodimethylsilyl)cyclohexane,

$Me_3Si\overline{N(CH_2)_3SiMe_2ClN}B\,{}^tBu$ (**V**). The trimethylsilyl derivative ($Me_3Si\overline{N(CH_2)_3N}HB^tBu$) (2.5 g, 11.78 mmol) in Et_2O (150 mL) was treated with BuLi (11.78 mmol, 4.7 mL of a 2.5 M solution) following the techniques described above. A solution of Me_2SiCl_2 (1.5 g, 11.78 mmol) in Et_2O (20 mL) was slowly added at 0 °C and the mixture left stirring overnight. The usual workup gave the product as colorless liquid with about 85% purity. B.P: 67-68 °C/0.01 mm Hg. Yield: 72%. δ ^{1}H: 0.15 (9H, $SiMe_3$, s), 0.46 (6H, MeSiCl, s) 0.92 (9H, ^{t}Bu, s), 2.9 (2H^a, t, J = 7.0 Hz), 1.58 (2H^b, m), 2.84 (2H^c, t, J = 6.0 Hz); δ^{13}C{H}: 3.54 (Me_3Si, s), 5.35 (SiMeCl, s), 30.99 (^{t}Bu, s), 43.81 (C^a, s), 29.72 (C^b, s), 41.81 (C^c, s).

1,3,2-diazabora-2-t-butyl-1,3-bis(dimethylsilyl)cyclohexane, $Me_2SiH\overline{N(CH_2)_3SiMe_2HN}B^tBu$ (**VI**). A solution of Me_2SiClH (3.6 g, 38.1 mmol) in Et_2O (20 mL) was slowly added to the dilithium derivative of made from **I** (2.5 g, 17.86 mmol) and the mixture left stirring overnight. The usual workup and distillation gave the analytically pure compound as a colorless liquid. B.P.: 50-52 °C/0.01 mm Hg; yield: 3.96 g, 85%. Anal., calcd.(found) for $C_{11}H_{29}BN_2Si_2$: C, 51.53 (50.82); H, 11.32 (11.70). δ ^{1}H: 0.09 (12H, SiMe, d, J = 3.1 Hz), 0.98 (9H, ^{t}Bu, s), 2.77 (4H, t, J = 5.7 Hz), 1.56 (2H, m), 4.77 (2H, SiH, sp, J = 3.2 Hz); δ ^{13}C{H}: -1.34 (SiMe, s), 31.29 (^{t}Bu, s), 43.09 (C^a, s), 29.54 (C^b, s), 43.28 (C^c, s).

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

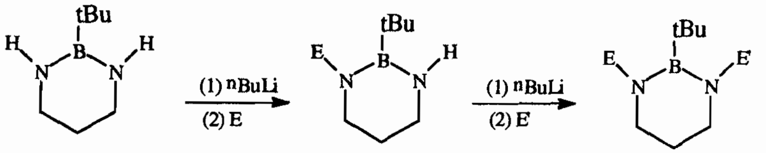
$Me_2HSi\overline{N(CH_2)_3SiMe_2NH_2N}B^tBu$ (**VII**). This was made from $Me_2Si(H)\overline{N(CH_2)_3SiMe_2ClN}B^tBu$ (1.8 g, 6.2 mmol) in hexane (15 mL) and NH_3 (31 mmol) following the procedure given for the synthesis of **IV**. Further workup gave a colorless and analytically pure compound. B.P.: 55-60 °C/2 mm Hg; yield: 1.2 g, 77%. Anal., calcd.(found) for $C_{11}H_{30}BN_3Si_2$: C, 52.54 (51.69); H, 10.12 (11.14). δ ^{1}H: 0.05 (6H, SiMeH, d, J = 3.2 Hz), 0.98 (9H, ^{t}Bu, s), 0.003 (6H, $SiMeNH_2$, s), 2.83 (2H^a, t, J = 5.2 Hz), 2.92 (2H^b, m), 1.58 (2H^c, t, J = 5.5 Hz), 3.04-3.12 (2H, NH, b), 4.86 (1H, SiH, sp, J = 3.3 Hz); δ ^{13}C{H}: -1.88 ($SiMeNH_2$, s), 4.26 (SiMeH, s), 29.45 (^{t}Bu, s), 40.24 (C^a, s), 28.09 (C^b, s), 41.97 (C^c, s).

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

$Me_2HSi\overline{N(CH_2)_3SiMe_2ClN}B\,{}^tBu$ (**VIII**). With a procedure similar to that for the synthesis of **V**, compound **II** (2.6 g, 13.13 mmol) in Et_2O (150 mL), BuLi (5.3 mL of 2.5 M solution, 13.13 mmol) and Me_2SiCl_2 (1.8 g,14.78 mmol) in Et_2O (10 mL) gave a pure colorless product. B.P.: 62-65 °C/1 mm Hg; yield: 3.3 g, 86%. Anal., calcd.(found) for $C_{11}H_{28}BN_2Si_2Cl$: C, 45.44 (43.96); H, 9.71 (10.01). δ ^{1}H: 0.45 (6H, SiMeCl, s), 0.11 (6H, SiMeH, d, J = 3.2 Hz) 0.95 (9H, ^{t}Bu, s), 4.95 (1H, SiH, sp, J = 3.2 Hz), 2.93 (2H^a, t, J = 7.3 Hz), 2.76 (2H^b, m), 1.61 (2H^c, t. J = 6.0 Hz), δ ^{13}C{H}: -1.59 ($SiMe_2H$, s), 5.02 (SiMeCl, s), 30.56 (^{t}Bu, s), 40.07 (C^a, s), 29.23 (C^b, s), 40.52 (C^c, s).

RESULTS AND DISCUSSION

The synthesis of the 2-t-butyl-1,3,2-diazaboralidene, $H\overline{N(CH_2)_3N}HB^{t}Bu$ (I), by the transamination of bis(dimethylamino)-t-butylborane and 1,3-propylene diamine is easy and gives a good yield [1]. The resultant compound (I) can be derivatized conveniently. The diazaboracyclohexane was deprotonated by treatment with an equimolar amount of n-BuLi and subsequent addition of the appropriate electrophiles (E and/or E') followed by filtration and vacuum distillation to give the desired products. Further deprotonation/substitution of the diazaboracyclohexane ring system may be accomplished by a similar reaction sequence (Scheme 1) to afford the disubstituted products.



E and E' are electrophiles

These compounds were obtained in good yields as colorless liquids and were characterized by elemental analyses and NMR spectroscopy (^1H, ^{11}B and ^{13}C).

The trimethylsilyl-substituted compound can be made only when the lithiation is done in the presence of one equivalent of TMEDA unlike all other syntheses which require lithiation of compound (I) in ether with one equivalent of n-BuLi at 0 °C for two hours followed by the addition of the electrophile.

Several attempts including using excess n-BuLi and Me_2SiHCl to prepare the disubstituted dimethylsilyl derivative gave mixtures containing about 8% of the monosubstituted (II) and 80% of the disubstituted compound that could not be separated by fractional distillation. Similarly for compounds with a phenyl substituent at boron it was reported that attempts to prepare the mono-HMe_2Si substituted compound gave mixtures of mono- and di-substituted derivatives that could not be separated by fractional distillation [5].

When compound **V** was treated with ammonia at -78 °C in hexane in an attempt to make the amino derivatives, compound **IV** was isolated in 28% yield and unidentified products with prominent peaks at δ -0.033, -0.026 and -0.01 in the ^1H NMR spectrum and at δ 1.26, 2.72 and 3.96 in the ^{13}C spectrum. However, when the same reaction was repeated with compound **VIII** the target product **VII**, together with unidentified products were observed. At present there is not enough evidence to explain these results.

The proton NMR spectrum of the compound (I) shows a well resolved triplet/quintet pattern for the trimethylene bridge. Upon monosubstitution, however, three distinct multiplets are observed, indicating the unsymmetrical structures of these derivatives. Also the non-equivalence of the carbon atoms adjacent to nitrogen is clearly apparent in the ^{13}C NMR spectrum. The ^{11}B NMR spectra of the compounds show signals close to each other (δ *ca* 30 for **I** and *ca* 34 for **II** to **VIII**) indicating little or no effect on derivatization.

Mono and disubstitution on the B-ring systems result in low field shift of the protons of t-Bu on the B atom. The methylene protons at position **a** moves to higher field but these are not apparent in compounds **II** to **IV**. Protons at position **b** have shown up field shift on substitution except for compounds **II**, **V** and **VI**. There is no noticeable chemical shift change of protons and carbons at position **c** upon substitution.

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