Bull. Chem. Soc. Ethiop. **2000**, 14(2), 123-128.
Printed in Ethiopia
ISSN 1011-3294

N-PHOSPHYL DERIVATIVES OF 2-t-BUTYL-1,3,2-DIAZABORACYCLOALKANE RING SYSTEM

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(Received April 11, 2000; revised July 1, 2000)

ABSTRACT. New mono- and disubstituted 2-t-butyl-1,3,2-diazaboracycloalkane, $\overline{EN(CH_2)_nE'NB}$^{t}Bu derivatives, [n = 3, E = H = E' (**I**), n = 2, E = E' = H (**II**), n = 3, E = H, E' = ^{t}BuPCl (**III**), E' = ^{t}BuPOCH$_2$CF$_3$ (**IV**), E' = Me$_2$PNSiMe$_3$ (**V**), E' = ^{t}BuPNMe$_2$ (**VI**), E = SiMe$_3$, E' = ^{t}BuPCl (**VII**), E' = OCH$_2$CF$_3$ (**VIII**), E = Me$_2$SiH, E' = ^{t}BuPNMe$_2$ (**IX**), n = 2, E = H, E' = ^{t}BuPCl (**X**), E' = ^{t}BuPNMe$_2$ (**XI**), E = Me$_3$Si, E' = ^{t}BuPCl (**XII**)], have been synthesized in good yield and characterized by spectroscopic and elemental analysis. ^{1}H, ^{13}C and ^{31}P NMR spectral data are analyzed and discussed.

INTRODUCTION

In recent years considerable number of small molecule boron-nitrogen compounds as potential precursors to B-N polymers, BN based ceramics and other solid state materials have been synthesized and reported [1]. As part of a continues work on the synthesis and characterization of N-boryl derivatives of 1,3,2-diazabora-2-t-butylcycloalkane ring system, as potential precursors for B-N polymers, we report here new N-phosphyl derivatives of 2-t-butyl-1,3,2-diazaboracycloalkane ring system.

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), ethylenediamine (Mallinckrodt), Me_3SiCl (Petrarch System Inc), Me_2SiHCl (Petrarch System Inc), PCl_3 (Aldrich), CF_3CH_2OH (Aldrich), 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.

$\overline{HN(CH_2)_nNHB}$^{t}Bu (n = 3) (**I**) [2] and n = 2 (**II**) [3] were prepared according to the known procedure. Proton and ^{13}C{H} spectra were recorded on a Varian XL 300 Spectrometer with $SiMe_4$ and $CDCl_3$, respectively, as references. ^{31}P{H} spectra were obtained on a JEOL FX 90 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

THIS PAPER IS DEDICATED TO COMOMORATE THE 50TH ANNIVERSASRY OF ADDIS ABABA UNIVERSITY

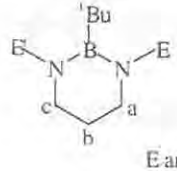
Procedure

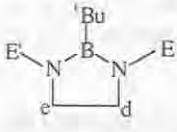
1,3,2-Diazabora-2-t-butyl-3-(t-butylchloro)phosphinecyclohexane, $HN(CH_2)_3P^tBuClNB^tBu$ (III). A 250 mL 3-necked flask equipped with dropping funnel, stirring bar and a septum was charged with the boron ring **I** (2.5 g, 17.9 mmol) in Et_2O (100 mL). nBuLi (17.9 mmol, 7.2 mL of 2.5 M solution in hexane) was added dropwise maintaining the temperature 0 °C, stirred for two h and for a further 2 h at room temperature.

^{t}BuPCl$_2$ (2.85 g, 17.9 mmol) in Et_2O (15 mL) was slowly added to the cooled solution (at 0 °C). The mixture was then left stirring overnight at room temperature, Et_2O was removed, the residue extracted with hexane, hexane stripped off from the filtrate and the residue distilled at 72-75 °C/0.01 mm Hg to give the analytically pure colorless liquid. Yield: 2.13 g, 45%. Anal., calcd (found) for $C_{11}H_{25}BClN_2P$: C, 50.32 (50.38); H, 9.60 (9.62). δ ^{1}H: 1.09 (9H, ^{t}BuP, d, J_{PH} = 14.2 Hz), 0.95 (9H, ^{t}BuB, s), 1.66 (1H^{a1}, (see footnote), m), 1.53 (1H, H^{a2}, m), 2.88 (2H^b, m), 3.43 (2H^c, m), 2.98 (1H, NH, m); δ ^{13}C{H}: 29.77 (^{t}BuP, d, J_{PC} = 12.8 Hz), 27.20 (^{t}BuB, s), 27.2 (C^a, d, J_{PC} = 20.9 Hz), 44.32 (C^b, d, J_{PC} = 4.2 Hz), 39.76 (C^c, s), 38.64 (PC, d, J_{PC} = 41.2 Hz); δ ^{31}P{H}: 157.0.

1,3,2-Diazabora-2-t-butyl-3-(t-butyltrifluoroethoxy)phosphinecyclohexane, $HN(CH_2)_3P^tBu(OCH_2CF_3)NB^tBu$ (IV). Similar procedure was followed to prepare the target compound from **I** (3.0 g, 21.4 mmol) in Et_2O (100 mL), 8.6 mL of 2.5 M nBuLi solution, (21.4 mmol), ^{t}BuP(Cl)OCH$_2$CF$_3$ (4.8 g, 21.4 mmol) in Et_2O (10 mL) to give analytically pure compound. B.p.: 65-66 °C/0.01 mm Hg; yield: 2.1 g, 30%. Anal., calcd. (found) for $C_{13}H_{27}BN_2POF_3$: C, 47.87 (47.58); H, 8.34 (7.74). δ ^{1}H: 0.99 (9H, ^{t}BuP, d, J_{PH} = 13.23 Hz), 3.90 (2H, OCH$_2$, m), 0.96 (9H, ^{t}Bu, s), 1.68 (1H^{a1}, m), 1.49 (1H, H^{a2}, m) 2.91 (2H^b, m), 3.2 (2H^c, m), 3.32-3.38 (1H, NH, b); δ ^{13}C{H}: 30.18 (^{t}BuP, d, J_{PC} = 12.2 Hz), 65.70 (OCH$_2$, dq, J_{PF} = 34.6, J_{PC} = 15.8 Hz), 124.39 (CF$_3$, dq, J_{PF} = 269.0, J_{PC} = 9.7 Hz), 35.63 (PC, d, J = 19.8 Hz), 27.08 (^{t}Bu , s), 43.97 (C^a, d, J_{PC} = 4.3), 29.49 (C^b, s), 39.70 (C^c, s), ^{31}P {H}.156.59.

1,3,2-Diazabora-2-t-butyl-3-[trimethylsilyl(dimethyl)]phosphoraneiminecyclohexane, $HN(CH_2)_3Me_2P(NSiMe_3)NB^tBu$ (V). Compound **V** was made from compound **I** (2.5 g, 17.9 mmol) in hexane (150 mL), TMEDA (17.9 mmol, 2.07 g) and nBuLi (17.9 mmol, 7.2 mL of 2.5 M solution in hexane) was added drop wise and the mixture was refluxed for 2 h. Me$_3$SiNP(Me$_2$)Br (4.1 g, 17.9 mmol) in hexane (10 mL) was added dropwise at room temperature. The mixture was allowed to stir overnight followed by reflux for 4 h. The usual work-up and distillation at 78-80 °C/0.01 mm of Hg gave the target compound as colorless liquid. Yield: 1.0 g, 20%. δ ^{1}H: -0.15 (9H, SiMe, s), 0.90 (9H, ^{t}Bu, s), 1.27 (6H, PMe, d, J_{PH} = 12.5 Hz), 1.42 (2H^a, m), 3.4-3.6(1H, NH, b); 2.85 (H^c, m), 1.62 (2H^b, m); δ ^{13}C{H}: 3.83 (SiMe, d, J_{PC} = 3.6), 29.83 (^{t}Bu, s), 20.14 (PMe, d, J_{PC} = 79.8 Hz), 43.22 (C^a, d, J_{PC} = 4.8 Hz), 27.19 (C^b, s), 39.60 (C^c, s), δ ^{31}P{H}: 17.4; MS: *m/z* 287(m$^+$), 272 (m$^+$- Me), 230 (m$^+$-^{t}Bu).





E and E' are electrophiles

1,3,2-Diazabora-2-t-butyl-1-trimethylsilyl-3-t-butylchlorophosphinecyclohexane,

$Me_2SiN(CH_2)_3P^tBu(Cl)NB^tBu$ (VI). A solution of butyllithium (11.78 mmol, 4.7 mL of a 2.5 M solution) was added to a mixture of the silylderivative of compound **I** [4] (2.5 g, 11.78 mmol) in hexane (100 mL) and TMEDA following the same procedure as described above. A solution of $^tBuPCl_2$ (1.87 g, 11.78 mmol) in hexane (10 mL) was slowly added to the mixture at room temperature and usual work-up gave a colorless liquid, b.p: 83-85 °C/0.01 mm Hg. Yield: 82%. Anal., calcd.(found) for $C_{14}H_{33}BN_2PSiCl$: C, 50.23 (49.99); H, 9.94 (9.99). δ ^{1}H: 0.11 (9H, $SiMe_3$, s), 1.06 (9H, ^{t}Bu, s), 1.05 (9H, ^{t}BuP, d, J_{PH} = 14.37 Hz), 1.30 ($1H^{a1}$, m), 1.75 (1H, ^{a2} m), 2.83 ($3H^{c1}$ and H^b, m), 3.44 ($1H^{c2}$, m,); δ ^{13}C{H}: 2.69 (Me_3Si, s), 29.32 (^{t}Bu, s), 31.65 (^{t}BuP, d, $^2J_{PC}$ = 13.7 Hz), 38.29 (PC, d, J_{PC} = 40.40 Hz), 31.65 (C^a, d, J_{PC} = 13.7 Hz), 44.26 (C^b, d, J_{PC} = 3.4 Hz), 44.18 (C^c, s). δ ^{31}P{H}: 147.39.

1,3,2-Diazabora-2-t-butyl-1-trimethylsilyl-3-(t-butyltrifluoroethoxy)phosphinecyclohexane,

$Me_2SiN(CH_2)_3CF_3CH_2O(^tBu)PNB^tBu$ (VII). A solution of $CF_3CH_2OP(^tBu)Cl$ (2.62 g, 11.78 mmol) in Et_2O (10 mL) was slowly added to the lithiated solution of the trimethylsilyl derivative of **I** [4] (2.5 g, 11.78 mmol) in Et_2O (100 mL). The usual work-up and distillation gave the analytically pure compound as a colorless liquid, b.p.: 77-78 °C/0.01 mm Hg; yield: 60%. δ ^{1}H: 0.10 (9H, SiMe, s), 1.06 (9H, ^{t}BuB, s), 0.95 (9H, ^{t}BuP, d, J_{PH} = 13.4 Hz), 3.94 (2H, OCH_2, dq, J_{FH} = 8.5, J_{PH} = 1.8), 1.27 ($1H^{a1}$, m), 1.77 (1H, H^{a2}, m), 2.85 ($2H^b$, m), 2.69 (1H, H^{c1}, dt, J_1 = 2.6; J_2 = 9.7), 3.26 (1H, H^{c2}, m); δ ^{13}C{H}: 2.59 (SiMe, s), 29.53 (^{t}Bu, s), 2.65 (^{t}BuP, d, J_{PC} = 18.4 Hz), 65.3 (CH_2, dq, J_1 = 3.5; J_2 = 15.3 Hz), 124.3 (CF_3, dq, J_{CF} = 4.7 Hz), 31.7 (C^a, d, J_{PC} = 13.0 Hz) 40.14 (C^b, d, J_{PC} = 2.3 Hz), 43.12 (C^c, s), 35.6 (PC, d, J_{PC} = 20.0 Hz); δ ^{31}P{H}: 148.4.

1,3,2-Diazabora-2-t-butyl-3-(t-butyldimethylamino)phosphinecyclohexane,

$HN(CH_2)_3{}^tBuPNMe_2NB^tBu$ (VIII). Compound **VIII** was made with 95% purity, based on the NMR spectroscopy analysis, from **I** (2 g, 14.3 mmol) in Et_2O (100 mL), BuLi (14.3 mmol) and ^{t}BuP(Cl)NMe_2 (2.5 g, 15 mmol) in Et_2O following the same procedure and work-up. B.p.: 67-68 °C/0.01 mm Hg; yield: 33%, δ ^{1}H: 0.93 (9H, ^{t}BuB, s), 1.0 (9H, ^{t}BuP, d, J = 12.7 Hz), 2.54 (6H, NMe, d, J = 9.5Hz), 1.6-1.7 ($2H^a$, m,), 3.15 ($2H^b$, b), 2.91 ($2H^c$, d, J_1 = 2.9; J_2 = 5.9 Hz), 2.63 (1H, NH, b). δ ^{13}C{H}: 29.61 (^{t}BuB, s), 29.4 (^{t}BuP, d, J = 18.8 Hz), 43.39 (NMe, d, J = 16.3 Hz), 30.2 (C^a, d, J = 12.00 Hz), 44.7 (C^b, d, J = 3.60 Hz), 40.2 (C^c, s), 35.5 (PC, d, J = 23.4 Hz). δ ^{31}P{H}: 108.7.

1,3,2-Diazabora-1-dimethylsilyl-2-t-butyl-3-(t-butyldimethylamino)phosphinecyclohexane,

$Me_2SiHN(CH_2)_3{}^tBuPNMe_2NB^tBu$ (IX). Compound **IX** was made from $Me_2SiHN(CH_2)_3{}^tBuBNH$ [4] (3.1 g, 15.66 mmol), in Et_2O (150 mL), BuLi (15.66 mmol) and $ClP(^tBu)NMe_2$, (2.6 g, 15.66 mmol) in Et_2O (10 mL) following the same procedure and work-up, in 88% purity. B.p.: 60-75 °C/0.01 mm Hg; yield: 33%, δ ^{1}H: 0.81 (9H, ^{t}BuB, s), 0.85 (9H, ^{t}BuP, d, J = 11.8 Hz), 0.01 (6H, MeSi, d, J = 3.3 Hz), 2.55 (6H, NMe, d, J = 6.4 Hz), 4.83 (1H, SiH, sp, J = 3.2), 2.88 ($2H^a$, m,), 1.54 ($2H^b$, m), 2.79 ($2H^c$, m),. δ ^{13}C{H}: 29.37 (^{t}BuB, s), 27.48 (^{t}BuP, d, J = 16.8 Hz), -1.97 (Me_2Si, s), 42.3 (NMe, d, J = 16.8 Hz), 41.87 (C^a, s), 40.15 (C^b, s), 27.48 (C^c, d, J = 13.3 Hz), 33.8 (PC, d, J = 18.8 Hz). δ ^{31}P{H}: 75.92.

1,3,2-Diazaboral-2-t-butyl-3-t-butylchlorophosphinecyclopentane,

$HN(CH_2)_2{}^tBuPClNB{}^tBu$ (X). The compound was prepared using the same technique from the boron ring [3] (2 g, 15.87 mmol) in Et_2O (100 mL), nBuLi (6.4 mL of 2.5 M solution, 15.87 mmol) and $^tBuPCl_2$ (2.5 g, 15.87 mmol) in Et_2O (20 mL). B.p.: 63-64 °C/0.1 mm Hg; yield: 38%. Anal., calcd.(found) for $C_{10}H_{23}BN_2PCl$: C, 48.33 (47.98); H, 9.33 (9.59). δ ^{1}H: 0.95 (9H, ^{t}BuB, s), 1.09 (9H, ^{t}BuP, d, J = 14.16 Hz), 3.63 ($1H^d$, m), 3.41($1H^d$, dt, J_{PH} = 0.9, J_{HH} = 9.8, J_{HH} = 7.6 Hz), 3.18 ($3H^c$ and NH, J_1 = 8.1, J_2 = 1.02 Hz). δ ^{13}C{H}: 28.81 (^{t}BuB, d, J_{PC} = 9.3 Hz), 26.70 (^{t}BuP, d, J = 20.00 Hz), 47.02 (C^d, d, J_{PC} = 8.0 Hz), 43.40 (C^c, s), 37.88 (PC, d, J = 35.1 Hz). δ ^{31}P{H}: 148.81.

1,3,2-Diazaboral-2-t-butyl-1-trimethyl silyl-3-t-butylchlorophosphinecyclopentane,

$Me_3SiN(CH_2)_2{}^tBuPClNB{}^tBu$ (XI). The compound was made from $HN(CH_2)_2NSiMe_3B^tBu$ [3] (2.2 g, 11.1 mmol) in Et_2O (150 mL), nBuLi (4.4 mL of 2.5 M solution, 11.1 mmol) and $^tBuPCl_2$ (1.7 g, 11.0 mmol) in Et_2O (20 mL) following the similar procedure as in the synthesis of compound **V**. B.p.: 80-81 °C/0.01 mm Hg; yield: 2.4 g, 76%, δ ^{1}H: 0.15 (9H, Me_3Si, s), 1.06 (9H, ^{t}BuB, s), 1.08 (9H, ^{t}BuP, d, J = 14.2 Hz), 3.59 ($1H^{d1}$, m), 3.10-3.25 ($3H^{d2}$, H^c, m); δ ^{13}C{H}: 3.73 (Me_3Si, s) 30.98 (^{t}BuB, d, J_{PC} = 12.7 Hz), 26.89 (^{t}BuP, d, J = 20.7 Hz), 47.07 (C^d, d, J_{PC} = 5.9 Hz), 50.30 (C^c, s), 38.10 (PC, d, J = 37.6 Hz). δ ^{31}P{H}: 149.21.

1,3,2-diazaboral-2-t-butyl--3-t-butyldimethylaminephosphinecyclopentane,

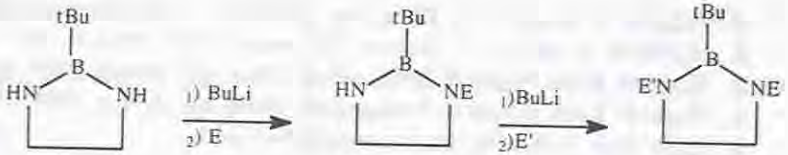
$HN(CH_2)_2{}^tBuPNMe_2NB{}^tBu$ (XII). The compound was made from **II** [3] (2 g, 15.8 mmol) in Et_2O (100 mL), BuLi (15.8 mmol) and $^tBu(Cl)PNMe_2$ (2.6 g, 15.80 mmol) in Et_2O (10 mL), after stirring for two days at room temperature and following the usual work-up gave an analytically pure compound. B.p: 83-85 °C/0.01 mm Hg. Yield: 82%. Anal., calcd.(found) for $C_8H_{22}BN_3PSiCl$: C, 48.01 (48.24); H, 11.00 (11.13). δ^{1}H: 0.92 (9H, ^{t}Bu, s), 1.01 (9H, ^{t}BuP, d, J_{PH} = 13.20 Hz), 2.6 (6H, NMe, d, J = 9.2 Hz), 3.08 ($2H^a$, dt, J_1 = 1.34, J_2 = 8.34 Hz), 3.5 ($2H^c$, m), 2.85 (1H, NH, b). δ ^{13}C{H}: 29.25 (^{t}BuB, d, J = 9.8 Hz), 25.80 (^{t}BuP, d, J_{PC} = 18.6 Hz), 43.70 (NMe_2, d, J = 17.00 Hz), 35.7 (PC, d, J_{PC} = 16.70 Hz), 49.28 (C^a, d, J_{PC} = 6.8 Hz), 43.68 (C^c, s). δ ^{31}P{H}: 102.00.

RESULTS AND DISCUSSION

Typically, the diazaboracycloalkane where n = 2 or 3 was deprotonated by treatment with an equimolar amount of n-BuLi at °C (see ref. 3 and 4). Subsequent addition of the appropriate chloro reagents followed by replacement of the Et_2O by hexane, filtration and vacuum distillation gave the compounds as colorless liquids. Further substitution of the diazaboracycloalkane ring system was accomplished by similar reaction procedure and sequence (see the reaction below for the cyclopentane ring system).

Almost all the compounds synthesized seem to be decomposing during distillation which probably is the major cause for the low yield (compounds, **IV**, **V**, **VIII** and **IX**) and purity of some of the compounds like in **V**, **VII**, **VIII**, **IX** and **XI**. For example, the crude compound **VIII** (before distillation) showed ^{31}P{H} signal at 109 ppm, however, after distillation a brown sticky substance was left in the pot with ^{31}P{H} at 113 (90%) and 116 (10%) after distillation. Similarly, three fractions were collected from the reaction mixture of compound

IX, wherein, fraction three (unidentified) remained as an impurity with the target compound. $^{31}P\{H\}$ of the residue in the pot after distillation showed peak at 113 ppm which corresponds to the familiar decomposition product of these type of compounds.



E and E' are electrophiles

The $^{31}P\{H\}$ NMR spectra consist of a single peak as expected in all the compounds and the chemical shifts are consistent (*ca* 148-157 ppm) indicating that the bonding of phosphorous to nitrogen and other groups in the 1,3,2-diazaboralidenes is more like that encountered in other similar compounds [5]. However, the phosphorus is more shielded in **VIII**, **IX** and **XII**, probably due to the presence of the electron rich ligand dimethylamine. The $^{31}P\{H\}$ of compound **V** is at 17.4 ppm signifying more shielding.

Interesting features in ^{1}H and ^{13}C spectra of the groups around phosphorus are also notable. $^{3}J_{PH}$ coupling and δ of ^{1}H NMR for the methyl protons of ^{t}Bu on P atom do not seem to vary much for both ring systems. $^{2}J_{PC}$ and δ of $^{13}C\{H\}$ of carbon of ^{t}Bu are close to one another in compounds **III**, **IV**, **VI**, and **VII** while δ of $^{31}P\{H\}$ in **VII**, **IX**, **X** and **XI** are relatively downfield with higher coupling constants. Another observation worth mentioning here is that the $^{4}J_{PC}$ coupling (4.3-12.7 Hz) of the P and methyl carbons on B atom, exists only in the five membered ring system signifying a closer proximity in the smaller ring systems.

The type of bonding, as revealed by ^{13}C, between the carbons of the ^{t}Bu directly bonded to phosphorus has a relatively higher order in compound **III** of the cyclohexane ring system than compounds **IV** to **IX**. The same observation was noted in compound **XII** of the cyclopentane ring system than **X** and **XII**.

The ^{1}H NMR of the compounds **VI**, **VII** and **X** consist of multiplets for each of the four protons at positions a, c, d, and e in the two ring systems featuring that they are magnetically non-equivalent. But in compounds **IV**, **III** and **IX**, the two protons at position a and d are in different environment may be due to sterric hindrance or existence of hydrogen bonding. Also, the $^{3}J_{PC}$ of the carbons are much lower in compounds **III**, **IX** and **X** while relatively higher in compounds **IV**, **VI** and **VII**. These compounds also show $^{4}J_{PC}$ (2.3-4.2 Hz) between P and C at position b, probably indicating significant overlap of orbital in this part of the ring. Doublet of quartets with J_{CF} (26.9-27.80 Hz) and $^{3}J_{CP}$ (9.7-4.7 Hz) is observed in the $^{13}C\{H\}$ NMR of compounds **IV** and **VII** demonstrating that phosphorus can couple through three bonds.

ACKNOWLEDGMENT

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

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