HETEROCYCLES, Vol. 86, No. 1, 2012, pp. 331 - 341. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 11th May, 2012, Accepted, 15th June, 2012, Published online, 18th July, 2012
DOI: 10.3987/COM-12-S(N)14

REACTION OF GRIGNARD REAGENTS WITH DIISOPROPYL-AMINOBORANE. SYNTHESIS OF ALKYL, ARYL, HETEROARYL AND ALLYL BORONIC ACIDS FROM ORGANO(DIISOPROPYL)-AMINOBORANE BY A SIMPLE HYDROLYSIS

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Abstract – Diisopropylaminoborane (BH_2-N(iPr)$_2$) is prepared by reacting lithium diisopropylaminoborohydride (iPr-LAB) with trimethylsilyl chloride (TMSCl). Aliphatic, aromatic, and heteroaromatic (diisopropylamino)boranes are readily synthesized at ambient temperature (0 °C) in 1 h by the reaction of Grignard reagents with (BH_2-N(iPr)$_2$). Two contending reaction pathways have tentatively been identified. During the mechanistic investigation, bromomagnesium diisopropylaminoborohydride was identified as a byproduct. This borylation reaction can be carried out under Barbier conditions, where (BH_2-N(iPr)$_2$) traps the in situ formed Grignard reagent from the corresponding organic halide and magnesium metal. Simple acid hydrolysis of the product organo(diisopropylamino)borane leads to the corresponding boronic acid in good to excellent yield.

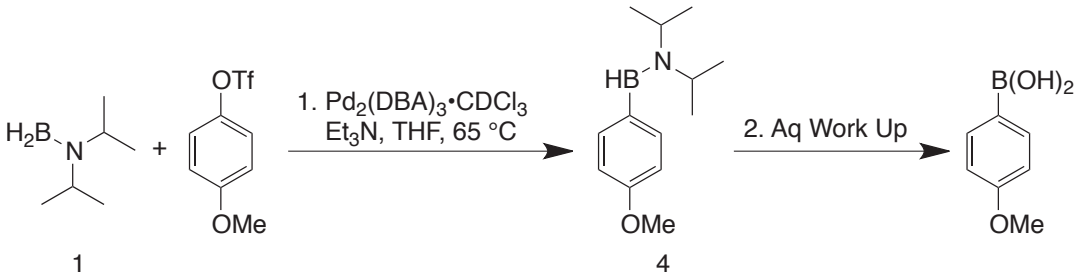
1. INTRODUCTION

In recent years interest in the chemistry of aminoboranes has increased dramatically mostly due to their potential application in hydrogen storage.[1-4] Aminoboranes (R_1R_2N–BH_2) are well-known in material science as precursors of BN-based ceramics.[5,6] The methods to synthesize aminoboranes include thermally induced dehydrogenation of secondary amine-borane adducts (R_1R_2HN:BH_3) and metal-catalyzed dehydrogenation of the corresponding amine-borane adducts.[7-10] Aminoboranes can also be synthesized by the reduction of the corresponding (amino)dihaloboranes.[11] Unfortunately, aminoboranes are known to form mixtures of dimers and oligomers, which prevented further

purification.[12] Consequently, they have been scarcely studied as useful tools for synthetic organic chemistry. It was recently shown that the monomeric dialkylaminoborane, diisopropylaminoborane (BH_2-N(*i*Pr)$_2$) **1**, can be used as an inexpensive boron source in palladium catalyzed Alcaraz-Vaultier borylation of aryl halides.[13] The BH_2-N(*i*Pr)$_2$ was prepared through thermal decomposition of the corresponding amine-borane at high temperatures with the concomitant generation of hydrogen gas.

Recently, we developed a mild and practical synthesis of various monomeric and dimeric aminoboranes from the corresponding lithium aminoborohydride (LAB) reagents and trimethylsilyl chloride (Scheme 1).[14] LAB reagents are prepared by deprotonating an amine-borane complex, H_3B:NHR_2, with *n*BuLi.[15] We reported that BH_2-N(*i*Pr)$_2$ prepared from the corresponding LAB reagent could also be used in the Alcaraz-Vaultier borylation (Scheme 1). The aryl(diisopropylamino)borane adduct **4** was not isolated but rather converted to the corresponding boronic acid upon acid hydrolysis.[14]

Scheme 1. In Situ Preparation of Diisopropylaminoborane from *i*PrLAB and TMS-Cl, Subsequent Palladium Catalyzed Borylation



1 4

We also reported that BH_2-N(*i*Pr)$_2$ is effective as a boron source for palladium catalyzed cross coupling with aryl iodides, bromides, and triflates.[16] Additionally, we found that BH_2-N(*i*Pr)$_2$ reduces nitriles at room temperature in the presence of catalytic amount of $LiBH_4$.[14,17]

However, very little is known about the reaction of aminoboranes with organometallic reagents, such as organolithium and Grignard reagents. Several years ago, Vaultier reported that Grignard reagents react with chlorobis(diethylamino)boranes to afford a mixtures of monoalkylbis(dialkylamino)boranes and dialkyl(diethylamino)boranes.[18] To the best of our knowledge there are no studies describing the reaction of organometallic compounds with BH_2-N(*i*Pr)$_2$. Consequently, we investigated the reaction of BH_2-N(*i*Pr)$_2$ with various organometallic reagents, such as butyl lithium, phenyllithium, phenylzinc bromide, and phenylmagnesium bromide. Herein, we report the results of our study on the reactions of various organometallic reagents with BH_2-N(*i*Pr)$_2$.

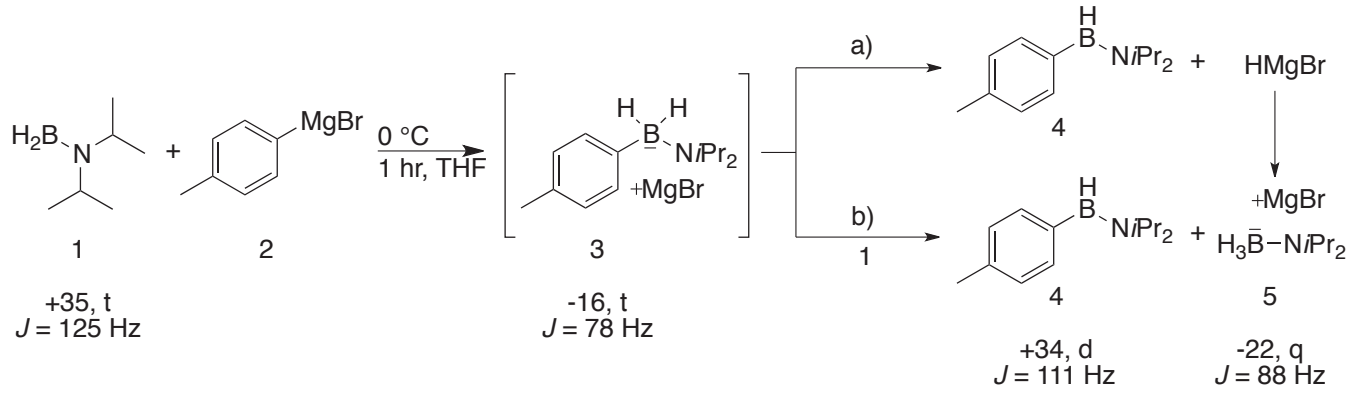
2. REULTS AND DISCCUSION

Diisopropylaminoborane BH_2-N(*i*Pr)$_2$ **1** was easily prepared by the reaction of the corresponding lithium

diisopropylaminoborohydride (LAB) reagent and trimethylsilyl chloride.[14] This reaction was quantitative as confirmed by ^{11}B NMR analysis, (δ +35, t, J = 125 Hz). We were interested in determining the compatibility of **1** with various organometallic reagents. When *n*BuLi was reacted with **1** in a THF solution, multiple additions were observed at both 0 and -78 °C according to ^{11}B NMR analysis. When the milder phenylzinc bromide was reacted with **1**, no addition was observed. Subsequently, the compatibility of Grignard reagents with **1** was investigated.

BH_2-N(*i*Pr)$_2$ **1** was reacted with one equivalent of *p*-tolylmagnesium bromide 2 at 0 °C in THF and the reaction progress was followed by ^{11}B NMR spectroscopy. After 30 minutes, ^{11}B NMR analysis revealed the absence of **1** (δ +35, t, J = 125 Hz) and the appearance of the single addition product aryl(diisopropylamino)borane (δ +38, d, J = 111 Hz) **4** and bromomagnesium aminoborohydride ($BrMgBH_3N(iPr)_2$, δ -22, q, J = 88 Hz) **5**.[21,19] The ^{11}B NMR spectrum also showed a small amount of the initially formed bromomagnesium aryl(diisopropylamino)borohydride adduct (δ -12, t, J = 78 Hz) **3**. Similar results were obtained when *p*-tolylmagnesium chloride was used (Figure 1).

A.



B.

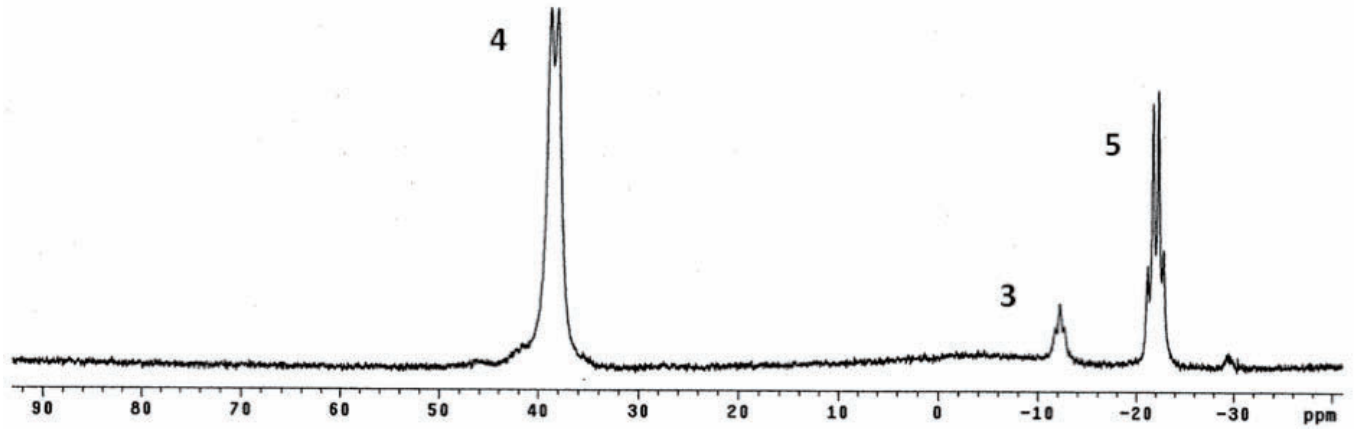


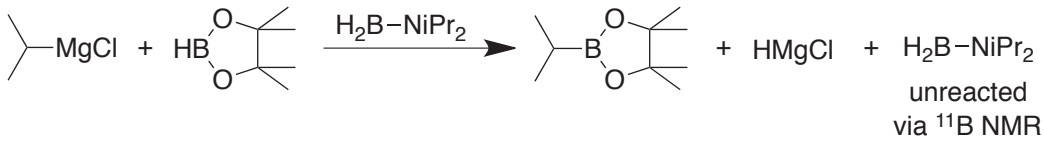
Figure 1. (A) Proposed Reaction Pathways. (B) ^{11}B NMR Spectrum of Reaction Mixture: Reaction conditions: *p*-tolylmagnesium bromide (1M/THF, 2.0 mmol) added to BH_2-N(*i*Pr)$_2$ (1M, 2.0 mmol) under argon at 0 °C, 30 min.

2.1 INVESTIGATION OF REACTION PATHWAY

A plausible mechanism of borylation involves an initial nucleophilic addition of **2** to the boron atom of **1** forming the bromomagnesium aryl(diisopropylamino)borohydride adduct **3**. Once **3** is formed it will either disproportionate forming **4** and hydridomagnesium bromide (HMgBr, Pathway A) or it can transfer a hydride to the starting material **1** forming **4** and **5** (Pathway B). Bromomagnesium diisopropylaminoborohydride **5** can also be formed by a simple addition of HMgBr to the starting material **1**.

HMgBr and HMgCl are known compounds and could be made essentially quantitatively from the reaction of isopropylmagnesium halide with pinacolborane in THF.[20] Unfortunately, HMgBr will disproportionate readily to $MgBr_2$ and MgH_2 in THF.[21] Fortunately, HMgCl, does not undergo disproportionation in THF. Consequently, we generated HMgCl in situ from isopropylmagnesium chloride and pinacolborane and reacted it with **1** to determine if HMgCl was capable of transferring a hydride to form chloromagnesium diisopropylaminoborohydride, an analog of **5**. Analysis of the reaction mixture by ^{11}B NMR spectroscopy showed the absence of any signals due to aminoborohydride. Due to an expected difference in reactivity between HMgCl and HMgBr this experiment is not conclusive, it does however, point out that the observed bromomagnesium diisopropylaminoborohydride may have resulted from a hydride transfer from intermediate **3** to **1** (Scheme 2).

Scheme 2. Attempted Reaction of hydridomagnesium chloride with BH_2-N(*i*Pr)$_2$



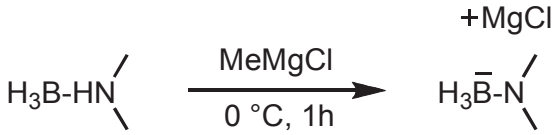
Interestingly, it was found that only 1.2 equivalents of **1** were required for greater than 95% conversion to the aryl(diisopropylamino)borane. This result strongly indicated that the reaction pathway did not exclusively proceed through Pathway B as two equivalents of BH_2-N(*i*Pr)$_2$ would be required to account for the quantitative conversion. Although the reaction mechanism is not fully understood we suggest that the reaction proceeds concomitantly through Pathways A and B.

2.2. SYNTHESIS OF CHLOROMAGNESIUM DIMETHYLAMINOBOROHYDRIDE

In order to verify the chemical shift and coupling constant of **5**, we attempted to synthesize authentic halo-magnesium aminoborohydride from diisopropylamine-borane and methylmagnesium chloride in THF. ^{11}B NMR analysis of the reaction mixture showed a small amount of the chloromagnesium aminoborohydride (δ -17, J = 88 Hz) and a number of disproportionation products. When the less

sterically demanding dimethylamine-borane was deprotonated with methylmagnesium chloride, chloromagnesium dimethylaminoborohydride (δ -16, J = 88 Hz) was produced quantitatively confirming the identity of **5** (see Supporting Information) (Scheme 3).

Scheme 3. Preparation of chloromagnesium aminoborohydride



2.3. HYDROLYSIS OF ORGANO(DIISOPROPYLAMINO)BORANE

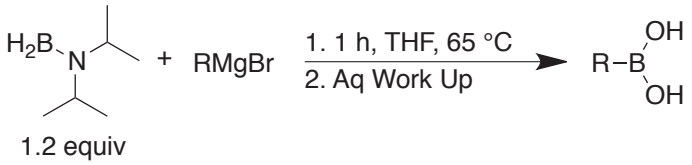
Previously, we have shown that aryl(diisopropylamino)borane compounds can be converted to the corresponding boronic acid via an aqueous quench.[20] ^{11}B NMR analysis of the water quenched reaction mixture showed the aryl(diisopropylamino)borane adduct and aminoborohydride peaks were replaced by a singlet (δ +30) and a quartet (δ -20, J = 98 Hz) corresponding to the boronic acid and amine-borane complex respectively. Although both the bromomagnesium aminoborohydride and the corresponding amine-borane reagents appear as sharp quartets with virtually identical chemical shifts in their respective ^{11}B NMR spectra, the coupling constants are significantly different.[22] The aminoborohydride reagent exhibits ^{11}B NMR J values of between 82-87 Hz. In contrast, the amine-boranes have coupling constants ranging from 95-98 Hz (See Supporting Information).[18] The boronic acid was then separated from the amine-borane by an acidic liquid-liquid extraction.

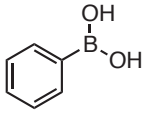
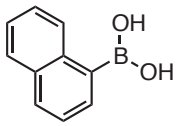
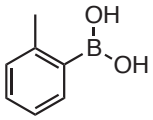
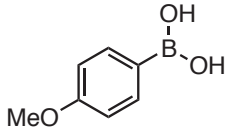
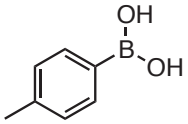
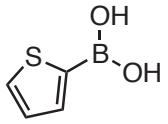
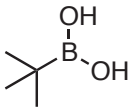
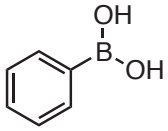
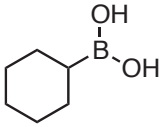
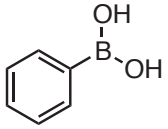
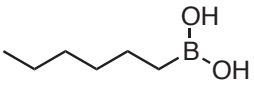
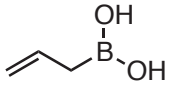
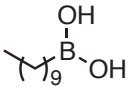
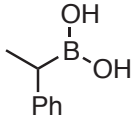
2.4. SYNTHESIS OF BORONIC ACIDS

We were pleased with the finding that organo(diisopropylamino)boranes can be converted to the corresponding boronic acid via an aqueous quench. Boronic acids have wide application in organic synthesis, especially in the formation of C-C bonds through the Suzuki-Miyaura cross coupling reaction.[23] The generality of the reaction of Grignard reagents with BH_2-N(iPr)$_2$ to generate aryl and alkyl(diisopropylamino)boranes was investigated by using commercially available, representative Grignard reagents.[24] The boronic acids, free of magnesium hydride and aminoborohydride, were readily isolated by quenching the reaction mixture with hydrochloric acid (3M) followed by diethyl ether extraction. This methodology was applied to a variety of aryl and alkyl Grignard reagents affording the corresponding boronic acids in essentially quantitative yields (Table 1). With preformed Grignard reagents the reaction was carried out at 0 °C for 1h (entry 1-7). It was interesting to find that phenylmagnesium bromide smoothly converted to the boronic acid in less than 30 min reaction time at

-45 °C (entry 11). This result implied that 1h of reaction time was not required at the reaction temperature of 0 °C. However, when the reaction was carried out at -78 °C (entry 12) the reaction mixture would freeze and magnetic stirring would stop. In this case, the reaction flask was removed from the cryogenic conditions, allowed to warm until the magnetic stir bar was free flowing and returned to the -78 °C conditions. Though the reaction was not maintained at a constant temperature the isolated yield of boronic acid was 95%.

Table 1. Synthesis of Boronic Acids Using Grignard Reagents[a] and Under Barbier Conditions[b]



Entry	Product	Yield[c] (%)	Entry	Product	Yield[c] (%)
1		95	8		79[b]
2		88	9		67[b]
3		95	10		74[b]
4		94	11		90[de]
5		97	12		95[fe]
6		78	13		<50[bg]
7		95	14		<50[bg]

[a]Reagents and conditions: BH_2-N(iPr)$_2$ (1M, 2.4 mmol), Grignard reagent (1M, 2.0 mmol), argon, 0 °C, 1 h. [b]Barbier conditions: Mg° (2.0 mmol), BH_2-N(iPr)$_2$ (1M/THF, 2.4 mmol), anhydrous THF (4.0 mL), organohalide (2.0 mmol), argon, 65 °C, 2-3 h. [c]Isolated yield of boronic acid after aqueous workup. [d]Reaction temp. -45 °C, [e]crude yield [f]reaction temp. -78 °C. [g]Conversion based on ^{11}B NMR.

Under Barbier-type conditions, a number of aryl halides underwent smooth conversion to the corresponding boronic acids with good yields. In this case the organic halide is added to a mixture of magnesium turnings and BH_2-N(iPr)$_2$ 1M/THF at 65 °C. The synthesis of boronic acids under the modified Barbier conditions was compatible with a number of arylbromides including 1-bromonapthalene (entry 8), 4-bromoanisol (entry 9) and the heteroaromatic 2-bromothiophene (entry 10). Other substrates, including α-bromostyrene and 9-bromoanthracene were not compatible with the Barbier conditions. When allyl and benzyl halides were subject to the Barbier conditions described above rapid consumption of the magnesium metal was observed. However, subsequent ^{11}B NMR analysis of the reaction mixture showed approximately a 1:1 mixture of the corresponding B-allyl(diisopropylamino)borane and unreacted BH_2-N(iPr)$_2$ (entry 13 and 14). What was observed was the rapid consumption of the magnesium metal and the presence of unreacted BH_2-N(iPr)$_2$ which can be explained by the homocoupling and reduction of the reactive allyl and benzyl bromides.

3. CONCLUSION

In summary, a simple and mild borylation of aryl and alkyl halides with BH_2-N(iPr)$_2$ has been described, under mild Grignard and Barbier conditions. It was found that Grignard reagents add only once to BH_2-N(iPr)$_2$. Performing the borylation reaction under Barbier conditions allows the use of a simple one-pot procedure and avoids low temperatures and expensive transition metal catalysts. Diisopropylaminoborane is inexpensively synthesized and is stable in THF for at least one year. The reaction proceeds in excellent yields, affords a single addition product under mild conditions and does not require excess of the boron donor. The organo(diisopropylamino)borane product is hydrolyzed under mild conditions to the corresponding boronic acid. Although the mechanism is not fully understood, we have tentatively identified two possible reaction pathways. In both cases, a hydride acts as a leaving group, either forming HMgBr (Pathway A) or adding to the starting material, BH_2-N(iPr)$_2$ (Pathway B). Evidence suggests that the reaction proceeds mainly through Pathway A, as only 1.2 equivalents of aminoborane is required for greater than 95% conversion to the aryl(diisopropylamino)borane. During the mechanistic investigation, bromomagnesium diisopropylaminoborohydride was identified as a byproduct and an analogue was subsequently synthesized from dimethylamine-borane and methylmagnesium chloride.

4. EXPERIMENTAL

General Methods.

All reactions were performed in oven-dried, argon-cooled glassware. The BH_2-N(iPr)$_2$ was used as synthesized; it was stored under Ar at room temperature. All Grignard reagents were used as received

from Aldrich, they were stored in the bottle received and kept in the refrigerator held at 15 °C. Magnesium metal was used as received from Aldrich. All air- and moisture-sensitive compounds were introduced via syringes or cannula through a rubber septum. Tetrahydrofuran (THF) was freshly obtained from a solvent purification system (Pure Solv MD, Innovative Technology Inc.). NMR spectra were recorded in $CDCl_3$. Chemical shifts are reported relative to TMS ($\delta = 0$) for ^1H NMR (500 MHz) and are referred to the $CDCl_3$ resonance ($\delta = 77$) for ^{13}C NMR (125.7 MHz) spectra. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), coupling constant and integration. Boron NMR samples were recorded at 160.4 MHz and are reported relative to external standard $BF_3{:}Et_2O$ ($\delta = 0$).

Synthesis of Bromomagnesium diisopropylaminoborohydride.

Methylmagnesium bromide (0.83 mL, 2.4 M solution in THF, 2.0 mmol) was cooled to 0 °C (ice bath). In a separate 25-mL round-bottom flask diisopropylamine-borane (0.118g, 2.0 mmol) was dissolved in anhydrous THF (2.0 mL). The diisopropylamine-borane/THF solution was added dropwise over 10 min via syringe at 0 °C to the methylmagnesium bromide/THF solution. After 0.5 h of stirring at 0 °C a 0.5 mL aliquot was analyzed via ^{11}B NMR, which showed the solution to be bromomagnesium diisopropylaminoborohydride (δ -22, q, $J = 83$ Hz).

General Procedure for the Preparation of Arylboronic Acids.

The following procedure for the preparation of *p*-tolylboronic acid is representative. A 50-mL round-bottom flask equipped with a magnetic stir bar and fitted with rubber septum was charged with BH_2-N(*i*Pr)$_2$ (2.4 mL, 2.4 mmol, 1.2 eq.). *p*-Tolylmagnesium bromide (2 mL, 2 mmol, 1 eq.) was added dropwise over 5 min via syringe while stirring at 0 °C (ice bath). After 1 h, with the reaction still on ice, 3M HCl (5 mL) was added dropwise over 5 min and allowed to stir for 30 min. The reaction mixture was transferred to a separatory funnel and extracted with Et_2O (2 x 15 mL). The organic layers were combined and washed with 1M HCl (4 x 15mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* (25 °C, 1 Torr) to afford *p*-tolylboronic acid as a white powder. For other boronic acids prepared by this method see Table 1.

General Procedure for the Preparation of Arylboronic Acids Under Barbier-type Conditions.

The following procedure for the preparation of 1-napthylboronic acid is representative. A 25-mL round-bottom flask equipped with a condenser and magnetic stir bar was charged with magnesium turnings (0.058 g, 2.4 mmol) and was activated by addition of iodine crystals and warming until iodine sublimed. The flask was cooled to 25 °C and was purged with argon. BH_2-N(*i*Pr)$_2$ (2.4 mL, 2.4 mmol) was added to the flask and brought to reflux. 1-Bromonapthalene (1.33 mL, 2.0 mmol) was then added dropwise over five minutes with constant stirring at 65 °C. The reaction was complete after 4 h as evidenced by the disappearance of BH_2-N(*i*Pr)$_2$ starting material (δ +35, t, $J = 125$ Hz), and the

appearance of a doublet at (δ 38, d, J = 112 Hz) with the corresponding bromomagnesium aminoborohydride signal ($MgBr^+$ $^-BH_3$-N*i*Pr_2, δ -28, q, J = 88 Hz). The reaction was then cooled to 25 °C and acidified with 3M HCl (3mL) (CAUTION: *hydrogen evolution*). After 10 min of stirring the reaction mixture was warmed to 65 °C and stirred for an additional 15 min. The reaction mixture was then transferred to a separatory funnel and extracted with Et_2O (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* (25 °C, 1 Torr) to afford napthylboronic acid as a white solid. The results for the other boronic acids prepared by this method are summarized in Table 1. For copies of the ^1H, ^{13}C and ^{11}B NMR spectrum see Supporting Information. Because of their facile dehydration, boronic acids tend to provide inconsistent melting points. Therefore, the melting points for boronic acids were not taken. (*J. Org. Chem.*, 2011, **76**, 3571.)

Phenylboronic acid (Table 1, entries 1, 11, 12);[16] White powder; (0.234 g, 95%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (t, J = 6 Hz, 2H), 7.61 (t, J = 7 Hz, 1H), 8.26 (d, J = 5.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d 128.0, 132.7, 135.7, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): d +30.7.

***o*-Tolylboronic acid** (Table 1, entry 2);[16] White powder; (0.226 g, 88%). ^1H NMR (500 MHz, $CDCl_3$): δ 2.82, 7.27 (m, 2H), 7.459 (dt, J = 1.5, 7 Hz, 1H), 8.22 (dd, J = 7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.1, 125.3, 130.7, 132.3, 137.4, 146.4; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +31.9.

***p*-Tolylboronic acid** (Table 1, entry 3);[16] White powder; (0.345 g, 95%). ^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.32 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.9, 128.9, 133.7, 135.9, 143.1, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.4.

***t*-Butylboronic acid** (Table 1, entry 4);[25] White powder; (0.481g, 94%). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.8, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +32.7.

Cyclohexylboronic acid (Table1, entry 5);[26] White powder; (0.497g, 97%). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.3, 27.5, 28.3, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.5.

***n*-Hexylboronic acid** (Table 1, entry 6);[27] White powder; (0.404g, 95%). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.7, 23.4, 24.2, 25.0, 32.5, 32.8; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +34.4.

***n*-Decylboronic acid** (Table 1, entry 7);[28] White powder; (0.888g, 95%). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.1, 22.7, 23.4, 24.4, 29.4, 29.5, 29.7, 31.9, 32.4, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.9.

1-Napthylboronic acid (Table 1, entry 8);[16] White powder; (0.253g, 79%). ^1H NMR (500 MHz, DMSO-d_6): δ 3.44 (brs, 1H), 7.50 (m, 3H), 7.78 (d, J = 5 Hz, 1H), 7.91 (t, J = 9.5 Hz, 2H), 8.36 (brs, OH),

8.42 (dd, *J* = 8 Hz, 1 Hz, 1H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 128.2, 128.8, 129.1, 132.0, 132.9, 135.7; ^{11}B NMR (160.4 MHz, DMSO-d_6): δ +30.2.

4-Methoxyphenylboronic acid (Table 1, entry 9);[16] White powder; (0.196g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 3H), 7.03 (d, *J* = 8.5 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 55.3, 113.7, 137.7, 163.4, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +29.1.

2-Thiopheneboronic acid (Table 1, entry 10);[16] White powder; (0.221g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 3.5, 4.5 Hz, 1H), 7.83 (d, *J* = 4.5 Hz, 1H), 8.06 (d, *J* = 4 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 128.9, 135.1, 139.8, carbon attached to boron not observed; ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +27.0.

Allylboronic acid (Table 1, entry 13);[29] ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +42.1 (d, *J* = 147 Hz), +36.6 (t, *J* = 129 Hz).

1-Boronic acid ethylbenzene (Table 1, entry 14);[30] ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +42.1 (d, *J* = 147 Hz, 1H), +36.6 (t, *J* = 123 Hz, 2H).

ACKNOWLEDGEMENTS

Dedicated to Professor Ei-ichi Negishi on occasion of his 77th birthday.

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