Convenient Preparation of Silylboranes

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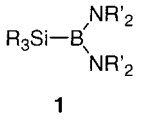
Summary: (Triorganosilyl)pinacolboranes were prepared by reaction of triorganosilyllithium reagents with pinacolborane or isopropoxypinacolborane in high yield. The reaction also is applicable to synthesis of 2-(triorganosilyl)-4,4,6-trimethyl-1,3,2-dioxaborinane. A new germylborane derivative was similarly prepared from the corresponding germyllithium.

Introduction

In recent years, additions of silylboranes to unsaturated organic molecules have been developed, leading to the synthesis of new organometallic compounds containing both silicon and boron.[1] Group 10 metal complexes have effectively activated the Si−B bond of the silylboranes, enabling regio- and/or stereoselective reactions with alkynes,[2] alkenes,[3] 1,3-dienes,[4] and 1,2-dienes.[5,6] Synthetic utility of the silylborane derivatives has been demonstrated by silaborative carbon−carbon bond forming reactions, which involve successive insertion of unsaturated molecules into the Si−B bond.[7]

Although compounds containing Si−B bonds have been known since 1960,[8] their reactivity has not been explored until recently, mainly due to the lack of synthetic accessibility of silylboranes. Although a series of silylboranes bearing two heteroatoms such as amino, alkoxy, and alkylthio groups on the boron atoms have been synthesized, use of chlorobis(dialkylamino)boranes is required for their preparation.[9] For instance, reaction of an organosilyllithium with chlorobis(diethylamino)-borane afforded (organosilyl)bis(diethylamino)borane **1**, which can be converted to the corresponding (organosilyl)dialkoxyborane as well as (organosilyl)di(alkylthio)-borane derivatives via ligand exchange reaction.[6a,10] (Organosilyl)pinacolboranes **2**, which have been employed in the recent silaboration chemistry, were prepared by this methodology.[2b] However, this method is not always convenient for practical use, since the preparation of chlorobis(dialkylamino)boranes can be difficult, especially due to their high moisture sensitivity. Therefore, development of a new and convenient preparation of silylboranes is desirable for further exploitation of their chemistry.



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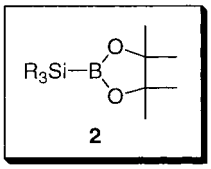

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In this paper, we disclose new preparative methods for the diol-derived silylboranes, in which easily accessible boron precursors are reacted with silyllithium reagents. The method was applied with good success to the synthesis of a related germylborane.

Results and Discussion

Reaction of Hydroboranes with Silyllithiums. Hydroboranes, $(R_2BH)_2$, are known to react with Grignard and organolithium reagents (R′M) to generate the corresponding organoborates ($MBR_2R'H$). Such borates can afford new organoborane compounds via elimination of the hydride on the boron atom as a leaving group.[11] However, substitution of hydride with silyl anions has never been achieved in a practical manner.[12] Attempted reaction of silyllithiums with 9-BBN (9-borabicyclo-[3.3.1]nonane) afforded bishydro- and bis(silyl)borate derivatives in high yield via disproportionation of the initially formed (hydro)(silyl)borate.[13] Nevertheless, we examined some reactions of cyclic hydroboranes with triorganosilyllithiums, since monohydroboranes with diol ligands such as pinacolborane **3** are easily accessible[14] and less susceptible to borate formation than 9-BBN.

Pinacolborane **3** was reacted with dimethylphenylsilyllithium in THF/hexanes (1/1) at 0 °C to room temperature. An initial attempt using 1 molar equiv of **3** resulted in the formation of the desired silylborane, but

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(12) Lippert, W.; Nöth, H.; Ponikwar, W.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 817.
(13) Biffer, W.; Nöth, H. *Angew. Chem.* **1980**, *92*, 65. Biffer, W.; Nöth, H. *Chem. Ber.* **1982**, *115*, 934.
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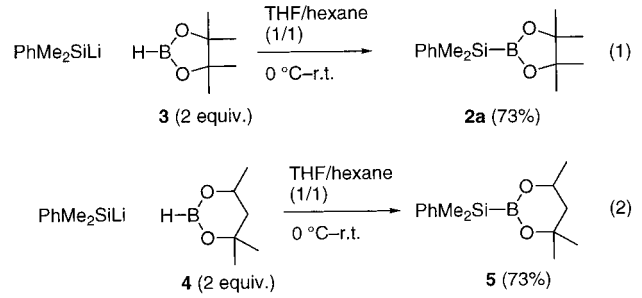
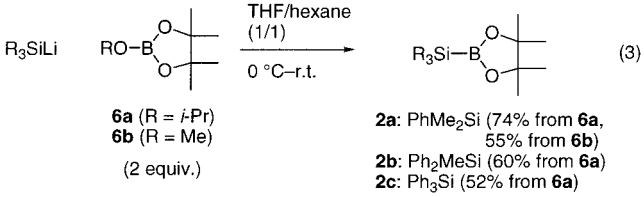
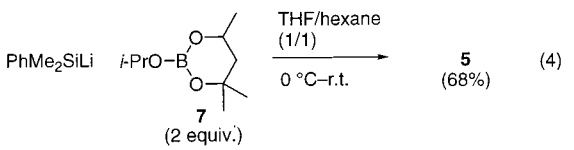
only in low yield. However, use of 2 molar equiv of **3** provided silylborane **2a** in 73% yield (eq 1).[15] The procedure was applicable also to the six-membered-ring hydroborane **4** for the synthesis of **5** (eq 2), but use of catecholborane failed to give the corresponding product at all. Under the same conditions, reaction of methyldiphenylsilyllithium with pinacolborane afforded the corresponding silylborane, which could not be separated from a small amount of byproducts.



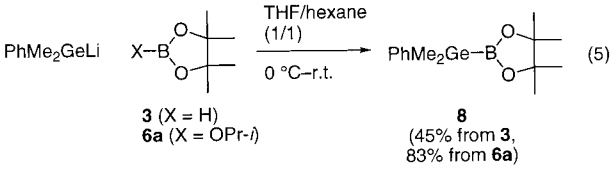
Reaction of Alkoxyboranes with Silyllithiums. The next candidates selected as potential starting materials in the silylborane synthesis were (alkoxy)pinacolboranes **6**, which are easily prepared by reaction of commercially available trialkoxyboranes with pinacol by heating.[16] In a manner similar to the reactions with hydroboranes, use of 2 molar equiv (rather than 1) of isopropoxypinacolborane (**6a**) with dimethylphenylsilyllithium gave a 74% yield of (dimethylphenylsilyl)pinacolborane **2a** (eq 3). Methoxypinacolborane (**6b**)



gave a lower yield (55%) for **2a** in the reaction with dimethylphenylsilyllithium under the same reaction conditions. In contrast with the silylborane synthesis with hydroboranes, the use of alkoxypinacolboranes was applicable to the synthesis of other silylborane derivatives. Indeed, methyldiphenylsilyl derivative **2b** and triphenylsilyl derivative **2c** were prepared by the reactions of **6a** with the corresponding silyllithiums in good yield (eq 3). Furthermore, six-membered ring derivative **5** was successfully prepared from the silyllithium and the corresponding isopropoxyborane **7** (eq 4).



Synthesis of Germylborane. Pinacolborane **3** as well as isopropoxypinacolborane **6a** served well as the boron sources in the preparation of the new germylborane **8**. Thus, reaction of isopropoxyborane **6a** with dimethylphenylgermyllithium provided (dimethylphenylgermyl)pinacolborane **8** in 83% yield, whereas use of the hydroborane **3** gave **8** in lower yield (eq 5).[17]



A reaction of trimethylstannyllithium with **6a** (2 equiv) was also attempted under the same reaction conditions as those for the preparation of the germylborane. However, no formation of the desired stannylborane was indicated by ^{1}H, ^{11}B, and ^{119}Sn NMR analyses of the reaction mixture. The analyses suggested that hexamethyldistannane with unidentifiable boron compound(s), which may have three oxygen substituents on the boron atom, was formed in the reaction.[18]

Conclusion

New synthetic routes to the silylboranes having diol ligands were established. The reaction of readily accessible boron sources, e.g., hydroboranes or, preferably, alkoxyboranes having diol substituents on the boron atoms, with silyllithium reagents gave synthetically useful silylboranes without difficulty. Application of this method to the synthesis of a germylborane was also successful.

The new method makes possible not only the practical utilization of the silylboranes but also their further development as powerful tools in organic synthesis.

Experimental Section

General Comments. All reactions were carried out under a nitrogen or argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-200 and a Varian Gemini 2000 equipped with 4.7 and 7.0 T magnets, respectively. Proton chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to internal residual $CHCl_3$ (7.26 ppm). Carbon chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the carbon signal of $CDCl_3$ (77.0 ppm). ^{11}B NMR spectra were recorded on a JEOL JNM-A400 equipped with 9.4 T magnet. The boron chemical shifts were referenced to the external standards $BF_3 \cdot OEt_2$ (0 ppm). Mass spectra were recorded on a JEOL JMS-HX100A or a JEOL JMS-SX102A.

THF and hexanes were distilled from Na/benzophenone and Na, respectively, under an atmosphere of nitrogen.

Dimethylphenylsilyllithium, methyldiphenylsilyllithium, and triphenylsilyllithium (ca. 1 mol/L in THF) were freshly prepared from the corresponding chlorosilanes with lithium (4 equiv) in THF. Dimethylphenylgermyllithium (0.75 mol/L in THF) was freshly prepared from chlorodimethylphenylgermane with lithium (4 equiv) in THF.[19] Pinacolborane (**3**),[14] 4,4,6-trimethyl-1,3,2-dioxaborinane (**4**),[20] isopropoxypinacolborane (**6a**),[16] methoxypinacolborane (**6b**),[16] and 2-isopropoxy-

(15) Lithium dihydro(pinacol)borate may inevitably be formed as a byproduct, although we have no evidence for it.

(16) Hoffmann, R. W.; Metternich, R.; Lanz, J. W. *Liebigs Ann. Chem.* **1987**, 881.

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(20) Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966**, *88*, 4667. We found that the method reported by Knochel (ref 14) was also applicable to the synthesis of this compound.

4,4,6-trimethyl-1,3,2-dioxaborinane (**7**)[16] were prepared according to the literature methods.

General Procedure for the Synthesis of Silylboranes. To a stirred solution of the hydroborane or alkoxyborane **3**, **4**, **6a**, **6b**, or **7** (128 mmol) in hexane (60 mL) was added dimethylphenylsilyllithium (ca. 1 mol/L in THF, 62 mL, 62 mmol) dropwise at 0 °C over 30 min. After the addition, the cooling bath was removed. The mixture was stirred overnight at room temperature. Evaporation of the volatile materials left white residual solid, which was taken up to remove material insoluble in hexane. After suction filtration under nitrogen, the filtrate was concentrated in vacuo. Distillation of the residue gave the silylborane as colorless liquid.

2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a). The title compound was prepared from **3**, **6a**, or **6b** and dimethylphenylsilyllithium according to the general procedure and isolated by distillation (97−99 °C/0.1 mmHg). For the title compound, only ^{11}B NMR resonance and the elemental analysis are given, since the same compound was synthesized previously and characterized, but without those descriptions.[2b] **2a**: ^{11}B NMR (C_6D_6) δ 34.3. Anal. Calcd for $C_{14}H_{23}BO_2Si$: C, 64.12; H, 8.84. Found: C, 63.83; H, 8.94.

2-(Methyldiphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b). The title compound was prepared from **6a** and methyldiphenylsilyllithium according to the general procedure and isolated by distillation (132−142 °C/0.2 mmHg). **2b**: ^{1}H NMR ($CDCl_3$) δ 0.61 (s, 3H), 1.28 (s, 12H), 7.30−7.36 (m, 6H), 7.56−7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −4.5, 24.9, 83.6, 127.8, 128.9, 135.0, 137.2; ^{11}B NMR (C_6D_6) δ 34.2; FABHRMS calcd for $C_{18}H_{22}BO_2Si$ [$M^+ - CH_3$] 309.1481, found 309.1474.

2-(Triphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c). A modified procedure was used for the synthesis of the title compound by reaction of **6a** with triphenylsilyllithium. After stirring overnight, the precipitate formed was filtered. Concentration of the filtrate gave a viscous oil, which gradually solidified on standing. The solid was washed with hexane and dried in vacuo to give **2c**. **2c**: mp 132.0−133.2 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 12H), 7.30−7.38 (m, 9H), 7.53−7.58 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 24.9, 83.9, 127.9, 129.1, 135.2, 136.2; ^{11}B (C_6D_6) δ 34.1; FABHRMS calcd for $C_{18}H_{22}BO_2Si$ [$M^+ - C_6H_5$] 309.1481, found 309.1494.

2-(Dimethylphenylsilyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (5). The title compound was prepared from **4** or **7** and dimethylphenylsilyllithium according to the general procedure and isolated by distillation (88−92 °C/0.6 mmHg). **5**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 6H), 1.19−1.30 (m, 9H), 1.51 (dd, J = 13.7, 11.7 Hz, 1H), 1.81 (dd, J = 13.7, 3.1 Hz, 1H), 4.06−4.25 (m, 1H), 7.26−7.36 (m, 3H), 7.55−7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.2, 23.1, 28.4, 31.2, 46.4, 64.2, 70.4, 127.5, 128.2, 134.3, 140.8; ^{11}B NMR (C_6D_6) δ 31.7; HRMS calcd for $C_{13}H_{20}BO_2Si$ [$M^+ - CH_3$] 247.1324, found 247.1313. Anal. Calcd for $C_{14}H_{23}BO_2Si$: C, 64.12; H, 8.84. Found: C, 64.06; H, 8.91.

Synthesis of 2-(Dimethylphenylgermyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). To a stirred solution of **6a** (17.7 g, 95 mmol) in hexane (60 mL) was added dimethylphenylgermyllithium (0.75 mol/L in THF, 60 mL, 45 mmol) dropwise at 0 °C over 30 min. After the addition, the cooling bath was removed. The mixture was stirred overnight at room temperature. Evaporation of the volatile material left a white residue, which was taken up in hexane. After suction filtration under nitrogen, the filtrate was concentrated in vacuo. Distillation of the residue (92−94 °C/0.6 mmHg) gave the germylborane **8** as colorless liquid (9.8 g, 83%). **8**: ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6H), 1.27 (s, 12H), 7.25−7.38 (m, 3H), 7.48−7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.9, 24.9, 83.8, 127.86, 127.89, 133.9, 141.6; ^{11}B NMR (C_6D_6) δ 35.4; FABHRMS calcd for $C_{13}H_{20}BGeO_2$ [$M^+ - CH_3$] 293.0767, found 293.0763.

Attempted Synthesis of a Stannylborane. To a stirred solution of **6a** (7.4 g, 40 mmol) in hexane (35 mL) was added a solution of trimethylstannyllithium (0.6 mol/L in THF, 33 mL, 20 mmol) dropwise at 0 °C over 30 min. The mixture was stirred overnight at room temperature. Evaporation of the volatile material left a residue, which was taken up in hexane. The suspension was filtered through a pad of Celite under nitrogen. The resultant filtrate was concentrated in vacuo. The presence of hexamethyldistannane was indicated by ^{1}H NMR (singlet at 0.20 ppm with satellites due to Sn−H couplings of 48.8, 46.4, and 15.8 Hz) and ^{119}Sn NMR (−109.6 ppm, $^1J_{Sn-Sn}$ = 4231 Hz). No bis(pinacolato)diboron (30.3 ppm), which may be formed in association with the formation of the distannane, was detected by ^{11}B NMR analysis (br s, 21.8 ppm).

Acknowledgment. We thank Mr. Akira Matsumoto for his assistance in the preparation of **2c**. T.M. thanks fellowship support from the Japan Society for the Promotion of Science for Young Scientists.

Supporting Information Available: ^{1}H and ^{13}C NMR charts for compounds **2a**−**c**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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