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A versatile synthesis of 9-BBN derivatives from organometallic reagents and 9-(triisopropylsilyl)thio-9-borabicyclo[3.3.1]nonane

John A. Soderquist * and Jorge C. Justo de Pomar †

Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931-3346, USA

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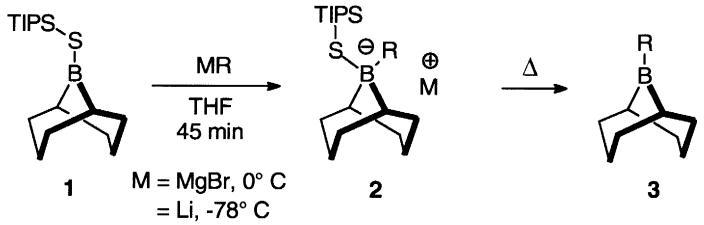
Abstract

Representative B-substituted-9-BBNs (**3**) are efficiently prepared from either organolithium or Grignard reagents through their addition to (TIPS)S-9-BBN (**1**) which is readily available from TIPSSH and 9-BBN-H. The thermally induced collapse of the intermediate 'ate' complexes (**2**) produces **3** which is easily isolated in good yield and high purity.



For many important organoborane conversions (e.g. Suzuki–Miyaura coupling),[1] the greater Lewis acidity of trialkylboranes compared to more oxygenated counterparts (e.g. $RB(OR')_2$) can be advantageous. Among these reagents, 9-BBN derivatives (**3**) are often the reagents of choice because of the robust nature of the 9-BBN moiety which functions efficiently as spectator ligation in many such transformations.[2] Hydroboration provides many of these derivatives, but for those which cannot be prepared by this method, several organometallic routes exist, the most straightforward being the addition of organolithium reagents to *B*-MeO-9-BBN in hydrocarbon solvents.[3a] In some cases (e.g. R=alkynyl), the intermediate 'ate' complex, Li[R(MeO)-9-BBN] is very stable and the addition of Lewis acids is required to produce **3**.[4] Unfortunately, with the exception of MeMgX, the analogous Grignard process is unworkable because the intermediate complex (M=MgX) decomposes too easily leading to di-addition (e.g. $M[R_2$-9-BBN]) and unreacted *B*-MeO-9-BBN.[3a] These complications and others[3b–d] limit the generality of the method and for a number of applications of **3**, it is preferable to either prepare

* Corresponding author.

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3 from 9-BBN-H and organocuprate reagents, or to generate **3** in situ from the exchange of *B*-Cl-9-BBN with $RSnR'_3$.[2,5]

We wish to report that (TIPS)S-9-BBN (**1**), which is easily prepared from 9-BBN-H and (TIPS)SH (1:1, 135–150°C (12 h), 85%, bp 143–146°C, 0.3 torr, ^{11}B NMR 81.7 (C_6D_6)),[7] provides a simple entry to **3** through both organolithium and Grignard procedures (Table 1).[8] With the exception of ViMgBr, the 1:1 adducts **2** are generally formed cleanly. Simply heating **2** under vacuum liberates **3**, which distills in pure form from the mixture (Table 1).[8] Acidification of the residue (HCl (aq.)) gives (TIPS)SH with a minor amount (~3%) of its hydrolysis product, TIPSOH.

Table 1
Representative *B*-R-9-BBNs (**3**) from **1**

Entry	M	R	Yield (**2**)[a]	δ ^{11}B NMR(**2**)[b]	Yield (**3**)[c]	Temperature[d] (°C, Torr)
1	MgBr	Me (**a**)	>98	-18.0	73	105, 15
2	MgBr	Et (**b**)	>98	-19.2	57	35-40, 3
3	MgBr	Ph (**c**)	>98	-16.7	90	100, 0.5
4	MgBr	cyclopropyl (**d**)	>98	-16.6	68	100-105, 3
5	MgBr	allyl (**e**)	>90	-24.4	60	85-90, 3
6	MgBr	vinyl (**f**)	[e]	[e]	25[e]	125, 3
7	MgBr	*n*-Bu (**g**)	>98	-15.3	82	105-110, 3
8	Li	*n*-Bu (**g**)	>98	-22.1	72	100, 0.3
9	Li	*t*-Bu (**h**)	>98	-16.8	71	52-60, 3
10	MgBr	1-hexynyl (**i**)	>85	-21.8	60	110-115, 0.1

[a] ^{11}B NMR yield based on conversion to **2**. [b] 96.3 MHz ^{11}B NMR in C_6D_6, referenced to BF_3-EE (δ 0.00 ppm). [c] Isolated yield of >98% pure material. [d] Distillation head temperature during thermal decomposition. [e] The low solubility of **2** in this case prevented its observation by ^{11}B NMR. Other species observed were **1** and the di-addition adduct.

In contrast to the behavior of **1**, the addition of BuMgBr to *B*-(*n*-PrS)-9-BBN (76.7)[6] at 0°C, from ^{11}B NMR analysis, gives a 1:1 mixture of unreacted *B*-(*n*-PrS)-9-BBN and MgBr[Bu_2-(9-BBN)] (−18.9). This reagent with *B*-(TIPSO)-9-BBN (57.1) produces ~1:1:1 mixture of this borate complex (−18.3), starting borane, and an intermediate complex assigned to the adduct (MgBr[(TIPSO)(Bu)-(9-BBN)] −17.9), which is converted to *B*-Bu-9-BBN (87.7) upon treatment with Me_3SiCl. Thus, the unique ability of the STIPS group to stabilize **2** is critical to the success of this new route to **3**.

Acknowledgements

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8. Representative procedures: (RLi) To a solution of **1** (1.24 g, 4.0 mmol) in dry ethyl ether (10 mL) at −78°C was added *t*-BuLi (3.4 mL, 1.6 M). After 45 min, concentration and distillation (head temp. 52–55°C, 3 torr) gave 0.50 g (72%) of **1h**. (RMgX) To a solution of **1** (1.52 g, 4.8 mmol) in dry THF (10 mL) at 0°C was added *n*-BuMgBr (2.75 mL, 2.0 M in THF) dropwise. After 45 min, the system was allowed to reach 25°C, the solvents were removed in vacuo, and heating as above (92–95°C at 5 torr) gave 0.72 g (84%) of pure **1g**.