Preparation of Dialkoxyborylbis(bromozincio)methane and Its Reaction with Electrophiles

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Dialkoxyborylbis(bromozincio)methane was prepared from dialkoxyboryldibromomethane by the Pb-catalyzed reaction with zinc. The dialkoxyborylbis(bromozincio)methane afforded vinylboranes by $TiCl_4$-mediated reaction with aldehydes or ketones. The reagent also coupled doubly with an equivalent organic halide under an influence of transition metal salts.

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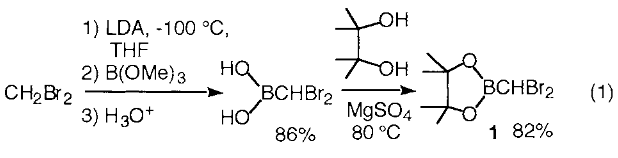
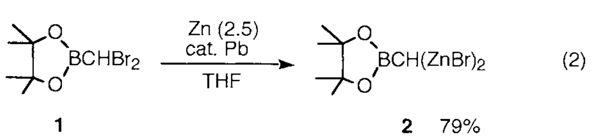
gem-Dimetallic reagents have attracted considerable attention as versatile reagents in organic synthesis.[1-3] Although various procedures have been contributed to the preparation of *gem*-dimetallic reagents, preparation and reaction of the simplest homologue of the reagents, dimetalomethane has not been extensively studied until our recent reports on the preparation and application of bis(iodozincio)methane.[3] Heteroatom-substituted ones have been expected to possess unique utility to construct functionalized molecules, and recently reported sily-substituted ones exemplified those synthetic utilities.[3d] The boron-substituted ones[4] are expected to give vinyl-, allyl-, and arylborane derivatives which are useful intermediate for organic synthesis.[5]

The boron-substituted *gem*-dizinciomethane was prepared from Zn and dialkoxyboryldibromomethane **1**. The compound **1** was prepared from dibromomethane according to the reported procedure[7] as shown in eq 1. The dihalide **1** was treated with zinc under an existence of catalytic amount of Pb.[3a,b,d] To a suspension of Zn (125 mmol) and $PbCl_2$ (15 mg) in THF (5 ml), **1** (5.0 mmol) in THF (1 ml) was added at 25 °C.[7] The mixture was sonicated for 10 min. To the mixture, being maintained at 60 °C, was added dropwise a THF (45 ml) solution of **1** (45 mmol) over 30 min. The resulting mixture was stirred for 1 h at the same temperature. The above procedure gave *gem*-dizinc compound **2** in 79% yield (eq 2).[8]





The boron-substituted dizinc reagent **2** reacted with carbonyl compounds **3** to yield alkenyldialkoxyboranes **4** (eq 3). Reaction with 3-phenylpropanal with **2** afforded **4** (R = $PhCH_2CH_2$, R' = H) in 42% yield and in 66% yield under an influence of $TiCl_2$. A use of $TiCl_4$ instead of $TiCl_2$ improved the yield to 70%. The stereoselectivity of **4** was shown in Table 1 (entries 1-3). In our report about methylenation of carbonyl compounds with bis(iodozincio)methane and titanium salt, $TiCl_4$ was shown to be reduced by bis(iodozincio)methane into divalent, and required a use of an excess amount of *gem*-dizinc reagent.[3b,d] In the present reaction, however, a use of even equimolar amount of **2** with $TiCl_4$ did not cause a lower yield of **4**. $TiCl_4$ was not reduced with the boron-substituted dizinc **2**, and played as a mediator as itself. Reactions of **2** with ketone was also tried (entries 6-9). Titanium salt mediated reactions gave the corresponding **4** from ketone. Without titanium salt or with a simple Lewis acid, BF_3•OEt_2, the reaction did not afford **4**.

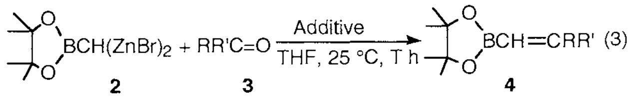
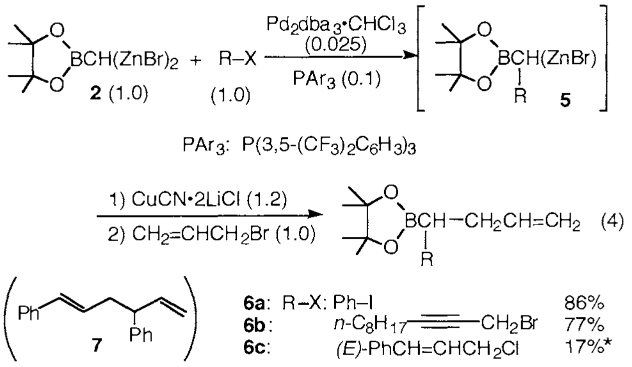


Table 1. Reaction with carbonyl compounds[a]

Entry	3	Additive	T / h	4 / %[b]	*E* / *Z*[c]
1	$PhCH_2CH_2CHO$	–	6	42	62 / 38
2		$TiCl_2$	3	66	85 / 15
3		$TiCl_4$	3	70	74 / 26
4	Dodecanal	$TiCl_4$	3	58	74 / 26
5	(*E*)-Cinnamaldehyde	$TiCl_4$	3	52	69 / 31
6	2-Dodecanone	–	12	<1	–
7		BF_3•OEt_2	12	<1	–
8		$TiCl_2$	5	46	54 / 46
9		$TiCl_4$	5	71	59 / 41

[a] **2** (1.0 mmol), **3** (1.0 mmol), and additive (1.0 mmol) were used. [b] Isolated yields. [c] The ratio was calculated based on ^1H nmr integral area.

A coupling reaction with organic halides under the influence of transition metal compounds was examined.[3c,d] As shown in eq 4, a reaction of **2** with iodobenzene under Pd catalyst gave boron substituted organozinc **5**; this compound reacted with allyl bromide under mediating with equimolar amount of copper salt.[9]



6a: R–X: Ph–I 86%
6b: n-C_8H_{17}–≡–CH_2Br 77%
6c: (*E*)-$PhCH{=}CHCH_2Cl$ 17%*
* **7** was obtained in 32% yield

Sequential reaction of **2** with propargyl bromide and allyl bromide afforded **6b** in 77% yield. A use of cinnamyl chloride accompanied a formation homocoupling diene **7**. The diene **7** supposed to be obtained via a formation of allyl zinc from allyl palladium and organozinc species **2**.[10]

The oxidation of C–B bond converts the product **6** into alcohol by a usual procedure for the oxidation of organoborane. For example, a treatment of **6a** with a mixture of 30% H_2O_2 and 1M aq NaOH in THF gave the corresponding alcohol quantitatively. The boron-substituted reagent possesses high reactivities towards electrophiles, such as carbonyl compounds, aryl halides, propargyl halides, and allyl halides. These results showed that our newly developed dialkoxyborylbis(bromozincio)methane functioned as hydroxymethylene dianion equivalent.

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7 Without $PbCl_2$, a commercially available Zn from Wako Pure Chemical, which is containing a small amount Pb, is effective. See, Ref 3a.

8 The yield of **2** was calculated from its concentration as a THF solution; The concentration was measured by ^{1}H nmr analysis using 2,2,3,3-tetramethylbutane as an internal standard. ^{1}H nmr (THF-d_8, 0 °C): δ -0.92 (s 1H), 1.14 (s, 12H) ppm.

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