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Simple procedures for the preparation of (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes

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Abstract

Two simple procedures for obtaining (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes based on 1-trimethylsilyl-1-alkynes are described. In the first procedure, 1-trimethylsilyl-1-alkynes are hydroborated with diisopinocampheylborane to provide the corresponding (*Z*)-2-(trimethylsilyl-1-alkenyl)-diisopinocampheylboranes. These are then reacted with excess acetaldehyde to afford the corresponding (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-diethoxyboranes which are esterified with 1,3-propane diol to give the (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes in good yields and in high stereochemical purities. In the second procedure, 1-trimethylsilyl-1-alkynes are hydroborated with dichloroborane–methyl sulfide complex in the presence of a stoichiometric amount of boron trichloride in hexane, followed by treatment with 1,3-propane diol. These novel stereodefined *gem*-alkenyldimetallic compounds containing boron and silicon are isolated and characterized by NMR (^{1}H and ^{13}C) spectral data. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: gem-dimetallic; stereospecific; diisopinocampheylborane; acetaldehyde; dichloroborane.

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1. Introduction

The syntheses of stereodefined alkenyl *gem*-dimetallic[1–7] compounds are well documented in the literature. The chemistry of *gem*-dimetallics containing boron and other metals is extremely useful in organic syntheses. The *gem*-dimetallics containing aluminum–zirconium,[1] zinc–zirconium[2] zinc–magnesium,[3] zinc–lithium,[3] zinc–boron,[4] copper–boron,[4] zirconium–tin,[5] boron–zirconium,[6] and boron–silicon[7] have been prepared and used in organic syntheses. However, not much attention is given to a study involving the isolation and characterization[8] of the stereodefined *gem*-alkenyldimetallics containing boron–silicon. Consequently, we wanted to undertake a stereospecific synthesis of an alkenyl *gem*-dimetallic compound such as the

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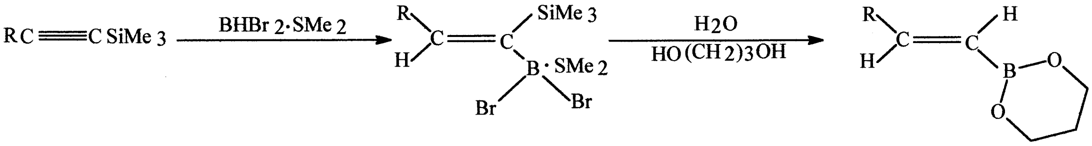
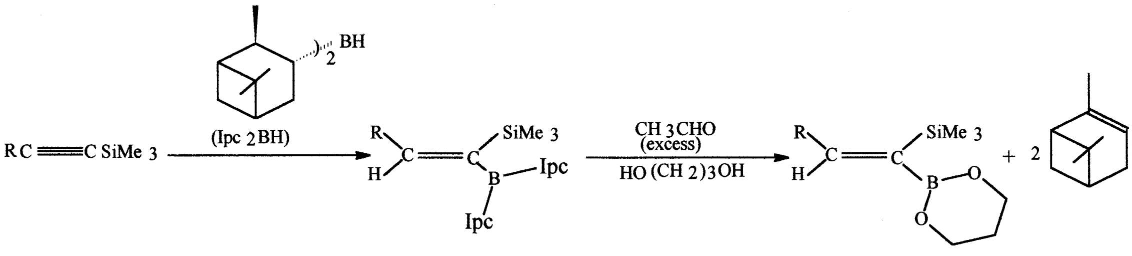
preparation of (*Z*)-2-(1-trimethylsilyl-1-hexenyl)-1,3,2-dioxaborinane via the hydroboration of 1-trimethylsilyl-1-hexyne with dibromoborane–methyl sulfide complex, followed by the reaction with 1,3-propane diol. To our surprise, we obtained desilylated product, as evidenced by NMR data (Scheme 1). The desilylation was presumably due to hydrogen bromide that was produced in aqueous medium during the course of the reaction. We overcame the desilylation reactions either by using hydrogen bromide free reaction medium utilizing dichloroborane–methyl sulfide complex as an hydroborating agent or by using diisopinocampheylborane which avoided the generation of hydrogen bromide or hydrogen chloride all together.

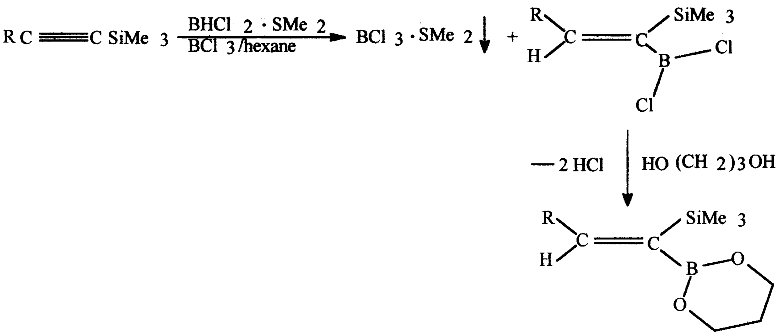


Scheme 1.

Consequently, we explored two different procedures (Schemes 2 and 3) to prepare (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes from 1-trimethylsilyl-1-alkynes. In this report, we would like to reveal the results of our investigation.



Scheme 2.

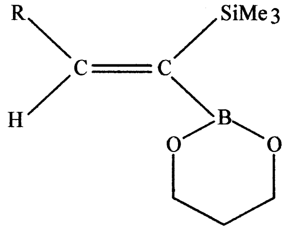


Scheme 3.

2. Results and discussion

In a typical first procedure,[9] 1-trimethylsilyl-1-hexyne (obtained from Aldrich Chemical Company) was hydroborated with diisopinocampheylborane[10] (prepared from (+)-α-pinene and borane–methyl sulfide in tetrahydrofuran) for 3 h. The resulting reaction mixture was reacted with a large excess of acetaldehyde[11,12] at 0°C for 1 h followed by reflux overnight. The resulting solution was connected to a high vacuum to remove (+)-α-pinene and the reaction mixture was dissolved in *n*-pentane. It was then transesterified[13] with 1,3-propane diol to provide (*Z*)-2-(1-trimethylsilyl-1-hexenyl)-1,3,2-dioxaborinane. It was isolated and characterized by PMR spectral data.[14] Using the above procedure, representative (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes (Scheme 2) were prepared (see Table 1).

Table 1
A novel synthesis of (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes



No.	R = [a]	% Yield[b,c] via $BHCl_2 \cdot SMe_2$	% Yield[b,c] via Ipc_2BH
1	-*n*-C_4H_9	72	82
2	-*n*-C_5H_{11}	75	78
3	-*n*-C_6H_{13}	70	84
4	-$C(CH_3)_3$	68	73
5	-$(CH_2)_3Cl$	65	72
6	-*sec*-C_4H_9	69	70

[a] All of the structures were confirmed by 300 MHz NMR (^1H and ^{13}C) spectral data.

[b] All of the reactions were carried out on a 10 mmol scale. The yields are isolated yields by high vacuum distillation.

[c] The carbon skeleton present in these intermediates was further confirmed by oxidation studies with alkaline hydrogen peroxide to the corresponding carboxylic acids.[7a]

In a typical second procedure,[15] 1-trimethylsilyl-hexyne was hydroborated[8] in pentane with dichloroborane–methylsulfide[16,17] complex at 0°C in the presence of a stoichiometric amount of boron trichloride in hexane for 3 h. The supernatant solution was then separated from the precipitated boron trichloride–methyl sulfide complex and the solution was treated with 1,3-propane diol at 0°C for an hour with stirring. The resulting product was isolated by high vacuum distillation (bp 94–96°C/0.01 torr) to provide the corresponding (*Z*)-2-(1-trimethylsilyl-1-hexenyl)-1,3,2-dioxaborinane in 82% isolated yield. Using the similar procedure, representative (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes (Scheme 3) were prepared (see Table 1).

3. Conclusions

In summation, we have developed two simple synthetic routes to prepare (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes from 1-trimethylsilyl-1-alkynes in good yields. The stereochemical purities[18] (>98%) of these versatile intermediates are determined by NMR spectral analysis. We are also currently exploring the synthetic applications of these promising stereodefined alkenyl *gem*-dimetallic intermediates by converting them into a variety of products. Consequently, the present potential intermediate will allow us to incorporate a trimethylsilyl group in a highly stereo- and regioselective manner in many organic structures via promising intermediates such as (*Z*)-2-(1-trimethylsilyl-1-alkenyl)-1,3,2-dioxaborinanes.

Acknowledgements

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15. Procedure for preparing (*Z*)-2-(1-trimethylsilyl-1-hexenyl)-1,3,2-dioxaborinane via dichloroborane–methyl sulfide complex is representative: In a 100 mL round bottom side-arm flask were placed 1-trimethylsilyl-1-hexyne (10 mmol, 2.0 mL) and *n*-pentane (10 mL). It was cooled to 0°C and then dichloroborane–methyl sulfide complex (10 mmol, 1.15 mL) was added at 0°C followed by boron trichloride (10 mmol, 1 M solution in hexane). The reaction mixture was stirred at 0°C for 3 h. The supernatant solution was then separated from the precipitated boron–methyl sulfide complex and the solution was treated with 1,3-propane diol (10 mmol, 0.72 mL) at 0°C for an hour with stirring. The solvents were removed using a vacuum and the resulting product was isolated by high vacuum distillation (bp 94–96°C/0.01 torr) to provide the corresponding (*Z*)-2-(1-trimethylsilyl-1-hexenyl)-1,3,2-dioxaborinane in 82% (1.70 g) isolated yield.

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