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A simple synthesis of *B*-2-(1-trimethylsilyl-1-alkyl)-1,3,2-dioxaborinanes. Isolation and selective oxidation to 1-trimethylsilyl-1-alkanols

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Abstract—(*Z*)-1-Trimethylsilyl-1-alkenes easily prepared by the hydroboration of the corresponding 1-trimethylsilyl-1-alkynes followed by protonolysis with acetic acid, readily react with dibromoborane-methyl sulfide complex in dichloromethane for 6 h. The resulting solution is then treated with 1,3-propane diol in a 1:1 mixture of dichloromethane and *n*-pentane at 0°C for half an hour to provide the corresponding *gem*-dimetalloalkanes containing boron and silicon. These alpha-trimethylsilylalkylboronate esters are purified by vacuum distillation in high yields (72–84%) and the structures of these novel intermediates are further confirmed by selective oxidation with alkaline hydrogen peroxide to provide the corresponding alcohols containing trimethylsilyl group.

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1. Introduction

Hydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane[1] is well documented in literature. The protonolysis of the resulting boron intermediates with acetic acid[2] provided the corresponding (*Z*)-1-trimethylsilyl-1-alkenes in high stereochemical purities. Different *gem*-dimetallics containing aluminum and zirconium,[3] zinc and zirconium,[4] zinc and magnesium,[5] zinc and lithium,[5] zinc and boron,[6] copper and boron,[6] boron and lithium,[7] and boron and zirconium.[8] Pelter and co-workers have reported an example of *gem*-dimetalloalkane containing boron and silicon.[9] Literature search revealed that no truly general simple synthetic procedures were available to prepare *gem*-dimetalloalkanes containing boron and silicon. Consequently, we undertook a methodology involving (*Z*)-1-trimethysilyl-1-alkenes via the hydroboration-alcoholysis sequence to achieve the synthesis of *gem*-dimetalloalkanes containing boron and silicon. In this report, we reveal the results of our investigation.

2. Results and discussion

We reacted terminal alkynes with *n*-butyllithium at −78°C for 1 h followed by treatment with chlorotrimethylsilane at −78°C for 1 h and allowed the reaction mixture to stir overnight. The resulting 1-trimethylsilyl-1-alkynes were isolated and kept in refrigerator under nitrogen atmosphere for further use. They were characterized by 300 MHz NMR spectral data.

The hydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane[10] (freshly prepared by mixing cyclohexene with borane–methyl sulfide complex) in tetrahydrofuran proceeded cleanly at 0°C, for 3 h followed by stirring for 1 h at room temperature. The resulting clear solution was treated with acetic acid and the stirring continued for 6 h at room temperature.

Table 1. Synthesis of 1-trimethylsilyl-1-alkenes

No.	Eq. (1) R =	Yield[a]
1	n-C_4H_9	82
2	n-C_5H_{11}	78
3	n-C_6H_{13}	86
4	$-(CH_2)_3Cl$	78
5	$-C(CH_3)_3$	76
6	-*sec*-Bu	79

[a] All of the reactions were carried out on a 50 mmol scale. The compounds were purified by chromatography over alumina followed by vacuum distillation.

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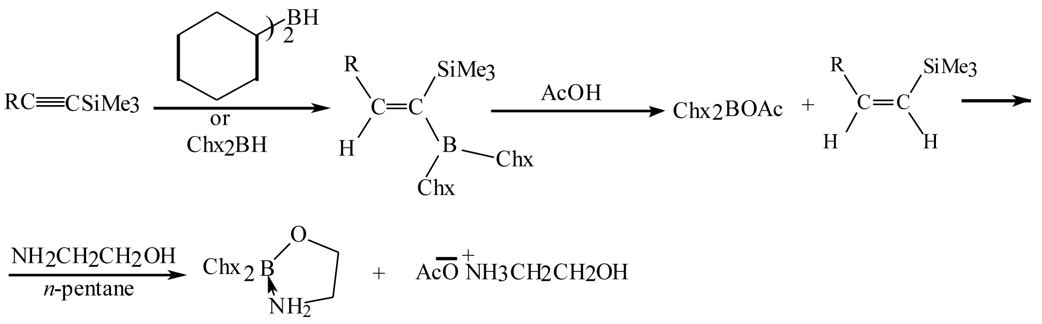
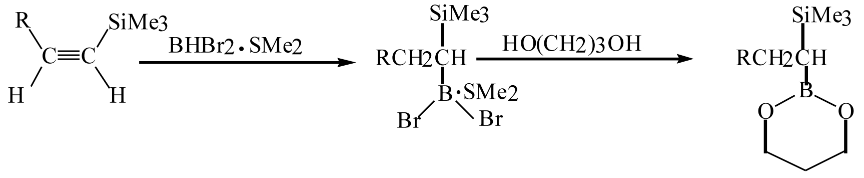


(1)



(2)

Table 2. The synthesis of *gem*-dimetalloalkanes containing boron and silicon

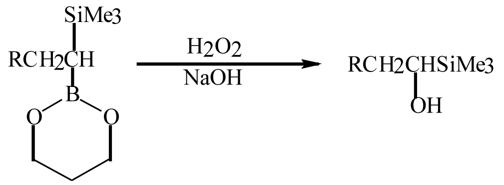
No.	Eq. (2) R=	Yield[a]
1	n-C_4H_9	84
2	n-C_5H_{11}	82
3	n-C_6H_{13}	78
4	-$(CH_2)_3Cl$	72
5	-$C(CH_3)_3$	74
6	-*sec*-Bu	80

[a] All of the reactions were carried out on a 10 mmol scale. The compounds were purified by vacuum distillation. The carbon skeletons present in these compounds were confirmed by selective oxidation to alcohols containing trimethylsilyl group (Eq. (3)).

The solvents were removed and replaced by *n*-pentane. Monoethanolamine[11] was added to remove the boron by-product. Representative (*Z*)-1-trimethylsilyl-1-alkenes (Table 1) were prepared (Eq. (1)) and characterized by 300 MHz NMR data.

The (*Z*)-1-trimethylsilyl-1-alkenes thus prepared were subjected to hydroboration with dibromoborane–methyl sulfide complex in dichloromethane at room temperature for 6 h. The resulting solution was reacted with 1,3-propane diol in 1:1 mixture of dichloromethane and *n*-pentane at 0°C for half an hour. The supernatant solution was removed by double-ended needle technique and the solvents were pumped off and the resulting liquids were purified by high vacuum distillation. The representative selection of *gem*-dimetalloalkanes were prepared (Table 2, Eq. (2)) using the above procedure.

These novel *gem*-dimetalloalkanes were reacted with alkaline hydrogen peroxide at room temperature for 3 h and the resulting alcohols containing trimethylsilyl group (Eq. (3)) were purified by column chromatography over alumina.



(3)

3. Conclusions

In summation, we have developed for the first time a simple, and efficient conversion of 1-trimethylsilyl-1-alkynes into the corresponding *gem*-dimetalloalkanes containing boron and silicon in high yields. These *gem*-dimetalloalkanes were isolated and characterized using 300 MHz NMR spectral data for the first time. The carbon skeletons present in these intermediates are further confirmed by selective oxidation studies with alkaline hydrogen peroxide to provide the corresponding alcohols containing trimethylsilyl group. We are presently utilizing these valuable compounds for further synthetic applications.

Acknowledgements

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